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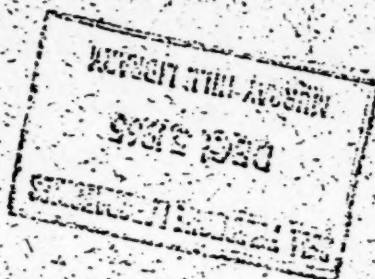
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NINETY YEARS OF A. M. BUTLEROV'S THEORY OF CHEMICAL STRUCTURE [1]

On September 19th 1861, 90 years ago, at a congress of German naturalists and medical men at Speyer in Germany, a young Russian chemist, Butlerov, read a paper entitled ''The Chemical Structure of Substances''. This paper marked the beginning of a new phase in chemical science and was a turning point in the development of theoretical concepts in organic chemistry. To me has fallen the great honor of delivering a discourse on the subject of this outstanding event in the history of chemistry.

Thinking over the question of how best to demonstrate the great significance of Butlerov' scientific feat, I came to the conclusion that I ought, as far as my time and knowledge permit, to unfold before you a picture of the theoretical views, particularly those within the realm of organic chemistry, which were dominant in the first and beginning of the second half of the nineteenth century among West European chemists, and, on this background, to portray the numerous obstacles and difficulties, and later struggle, which Butlerov had to withstand and overcome, before his brilliant theory of the structure of organic compounds obtained the rights of citizenship and became embodied in science.

At the beginning of the last century, the electrochemical theory of Davy and Berzelius held sway among chemists everywhere, and it may certainly be considered that the electrochemical theory embraced all the types of chemical compound known at that time. In Berzelius's opinion, every chemical compound could be imagined to consist of two oppositely charged parts, and, in particular, in such typical cases as the alkali salts of strong acids, there were to be distinguished in the make-up of the compound a negatively charged part, or acid, such as SO_3 (by an acid Berzelius understood what we should now call an acid anhydride), and a positively charged base, such as K_2O. On Berzelius's theory, an acid must contain oxygen, which was then regarded as the most electronegative element. However, already in 1810, Davy failed to detect oxygen in the composition of halogens, which, nevertheless, formed real salts.

A powerful blow was dealt to the electrochemical theory of Berzelius by the work of the French chemist Baptiste Dumas, who in 1834 discovered that in organic compounds, particularly in organic acids, such as acetic acid, one, two, or three proportions of electropositive hydrogen could be replaced by one, two, or three proportions of electronegative chlorine, without essential change in the character of the compound. This phenomenon received the name of metalepsy (i.e.,

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substitution – Translator). At the same time, this reaction served Dumas as a starting point for the creation of the so-called theory of types. As is well known, Dumas distinguished chemical types and mechanical types. It may be noted that Dumas' right to priority for the discovery of the metalepsy reaction was disputed by the French chemist Laurent.

It is appropriate here to draw your attention to the difficulty with which new facts and new views become accepted in science and to the obstinacy with which supporters of the old views, in this case the eminent Swedish chemist Berzelius, defended their scientific theories and convictions. For a long time, Berzelius, in spite of the evidence, resolutely denied the resemblance in type between acetic and trichloroacetic acids, pointing out that with respect to their physical properties these compounds do not resemble one another in the slightest degree. To this, as it seemed to Berzelius, substantial objection Dumas replied in an article in which, among other things, he wrote: "I have known for a long time that replacement of hydrogen in a volatile compound by chlorine makes the substance specifically heavier, less volatile, and possessed of a denser vapor, it is clear therefore that Berzelius's objections are not relevant to the view I have expressed".

Also, Dumas wrote in his article: "I have observed a very remarkable reaction when any alkali acts on trichloroacetic acid: the acid breaks down into two bodies, carbonic acid, which unites with the alkali, and free chloroform. . . . I was convinced and even predicted in my memoir that acetic acid would be capable of an analogous reaction, i.e., that under the action of excess alkali it would be converted into carbonic acid and a hydrocarbon of formula C_4H_8" (in modern language CH_4, or methane – A.E.A.). "This means," Dumas remarks further, "that acetic acid and trichloroacetic acid have analogous properties. . . . and belong to the same organic type". [1]

Extending the concept of substitution, Dumas considered it probable that hydrogen in organic compounds could be replaced not only by chlorine or other elements, but also by complex groups, i.e., radicals, which in these cases play, as it were, the part of actual elements. Later, Dumas came to still wider conclusions.

"Until now," wrote Dumas, "I have argued as if the substitution law could be actually applied only to the replacement of hydrogen, which was indeed the first to be observed. . . ., but it sould be noted," Dumas writes further, "that also carbon . . . and consequently all elements in an organic compound may be successively displaced and replaced by others".

It must be remarked here that this hyperbolical generalization of Dumas was at the time subjected to harsh and even humorous criticism (I am thinking here of Wöhler's well known letter), but the very fact that some elements may be replaced by others served as a fresh starting point in the development of theoretical ideas in chemistry. For the further development of theoretical ideas in chemistry, particularly in organic chemistry, science is indebted to the French chemists Gerhardt and Laurent. In 1841, Gerhardt obtained the chair of organic chemistry at Montpelier, and, faced with the task of expounding organic chemistry to a student audience, he must have met with all those difficulties that were bound to present themselves to every teaching chemist at that period in the evolution of organic chemistry, when, as a result of the rapid development in pre-

[1] Comptes rend. 9 (1839); Comptes rend. 10, 149-178 (1840).

parative synthetic chemistry and of the multitude of new compounds that had been prepared and of new facts that had been discovered, there was a mass of accumulated material that could not be brought within the scope of the prevailing dualistic theory of Berzelius.

The basic problems and aims of research chemists were formulated by Gerhardt in the following words: "Chemistry concerns itself with the changes of matter; its attention is focused on transformations — it is here that its essential nature lies; it investigates the origin of substances; it records their past and indicates their future; it keeps track of a substance through its various phases until its return to its original state — I do not say 'until its end,'" remarks Gerhardt, "because it has no end. Matter is not destructible, it only changes." (Introduction a la chimie unitaire.)

Gerhardt's great service in the development of theoretical chemistry was the delimiting of the concepts of atom, particle (i.e., molecule — Translator), combining weight, and equivalent. Before Gerhardt's time, chemists had attributed atomic weights to the various elements in rather arbitrary fashion; thus, for oxygen some assumed the atomic weight to be 8, while others assumed it to be 16, atomic weights of 6 and 12 were quoted for carbon, and so on. This confusion was, of course, reflected also in the representation of the formulas of compounds. Gerhardt shared the honor of establishing these most important concepts of chemistry with his friend and supporter Laurent, who must be given the credit for the important idea of taking the volume occupied by a definite amount of a substance in the gas or vapor state as the unit for comparison, following the Avogadro-Ampere hypothesis.

When discussing the establishment of the distinction between the concepts of atom, particle, and equivalent, chemical historians nearly always mention the names of these two French chemists together. It is necessary to add that their work of reforming the whole of chemistry had also its weak aspects, particularly in connection with the determination of the atomic weights of the alkali metals, silver, etc.

The impossibility, with the experimental technique existing at the time, of comparing in the vapor state the volumes of alkali metal or silver compounds with the volumes of compounds of other elements led Gerhardt and Laurent to propose incorrect values for the atomic weights of many elements. This circumstance greatly undermined the faith of chemists in the usefulness of the reform proposed by Gerhardt and Laurent. Later, the above-mentioned difficulties were overcome by the Italian chemist Cannizzaro, who, in the estimation of the atomic weights of the metals, made use of vapor density determinations on certain of their volatile compounds and also of the law of Dulong and Petit.

At an international congress of chemists at Karlsruhe in September 1860, i.e., a year before Butlerov read his paper at Speyer, a communication was made by Cannizzaro, and a resolution was then passed in which principles were laid down for the delimitation of the concepts of atom, particle, and equivalent. The atomic weights proposed by Cannizzaro for the elements were accepted by the great majority of chemists and have been firmly embodied in chemical science from that time on.

The distinction between the concepts of atom and particle established by Gerhardt and Laurent and the replacement of a four-volume formula by a two-volume formula made it possible for these reformers to alter the formulas of an enormous number of substances and, on the basis of the substitution phenomena discovered by Dumas, to declaim energetically against the dualistic concepts of Berzelius. The subsequent application by Gerhardt of the new particle concept led him to the

creation of the so-called unitary system or theory.

The unitary system and the new particle weights made it impossible to apply Berzelius's dualistic formulas to such compounds as nitric acid, the caustic alkalis, and many others. Radicals, which on earlier views could exist as separate particles (compounds), were represented according to the new views as groups of atoms, which could go from one compound to another, or could replace individual elements.

The phenomenon of substitution and the new concept of radicals enabled Gerhardt, and at the same time Williamson, to regard complex compounds as derivatives of simpler ones. From this arose the so-called theory of types, which aided the development of synthetic organic chemistry to an extraordinary extent.

May I draw your attention to yet another chemical phenomenon — that which has come to be called isomerism. At the beginning of the nineteenth century, even such great thinkers as Berzelius supposed that the properties of chemical substances were entirely determined by their compositions. Hence, when in 1824 Liebig and Wohler established the composition of silver fulminate and so the composition of fulminic acid and Wohler showed by exact analysis that cyanic acid has the same composition as the fulminic acid of Liebig and Gay-Lussac, this new phenomenon drew very great attention from chemists.

On this occasion Berzelius announced categorically that the cause of the inexplicable coincidence must be sought in inaccurate analysis. At first Liebig held the same view. Later, however, Liebig himself confirmed by analysis the identity in composition of the salts of fulminic and cyanic acis. Very quickly, examples similar to that cited began to multiply, and Berzelius himself acknowledged the existence of a new phenomenon and gave it the name "isomerism." I do not need to go into further details, but will mention only that some time passed before chemists distinguished the phenomenon of isomerism from polymerism and metamerism. The phenomenon of isomerism, as we can now well understand, was bound to play, and in fact did play an important role in the development of the theory of the structure of organic compounds.

The next stage, which brought chemists nearer, first to setting, and then to solving problems on the structure of organic compounds, was the theory of the atomicity of elements (valency). The honor of establishing the concept of valency belongs to the English chemist Frankland, who, already in 1852, established that "no matter what the character of the uniting atoms may be, the combining power of the attracting element is always satisfied by the same number of these atoms."

Although, in the first place, Frankland established this law for inorganic compounds — compounds of nitrogen, phosphorus, antimony, arsenic, and tin — the German chemist Kolbe, on the basis of some very original and unusual considerations, later (1857) extended Frankland's idea to carbon and so acknowledged carbon as a quadrivalent element, admitting, however, at the same time that there are cases of bivalent carbon, e.g., in carbon monoxide, and even cases of tervalency.

Independently of Kolbe, the German chemist Kekule in the same year, 1857, starting from quite different premises, also arrived at the idea of the valency of the elements, and also recognized the quadrivalency or tetrabasicity of the carbon atom, citing as the simplest examples the formulas of methane and carbon tetrachloride; at the same time, he assumed the atomic weight of carbon to be 6. In the next year, 1858, Kekule made the extremely important step of extending the quadrivalency of carbon to compounds containing several carbon atoms and so came to the idea of the chaining together of carbon atoms in these compounds.

In his article "The Constitution and Metamorphoses of Chemical Compounds, and the Chemical Nature of Carbon" Kekule wrote: "for substances containing several carbon atoms, it is necessary to assume that at least some of the atoms are held in combination by the combining power of carbon and that the carbon atoms are themselves united one to another, part of the combining power of one of them being, of course, bound up with the same proportion of the combining power of another." This rule for the chaining together of carbon atoms Kekule extends also to cases in which carbon atoms are combined with other multivalent elements, e.g., in the simplest cases, oxygen and nitrogen.

Here I approach the most important point of my discourse — the question of what chemists of that time thought of the possibility of representing the internal structure of chemical molecules in formulas. It will be obvious that in my short historical sketch I have not said much owing to lack of time and to the wideness of the subject.

The evolution of chemistry, particularly organic, in the period prior to the creation of the theory of chemical structure by Butlerov, proceeded by a more complicated path than that which I have portrayed above. It will be sufficient here to mention the experimental investigations of Williamson on the formation of ethers and the investigations of Gerhardt on the formation of the anhydrides of organic acids, which led to the acceptance of a molecular formula for these substances that was doubled with respect to that previously accepted.

The development of ideas concerning the polybasicity of acids by Berzelius and Liebig and of ideas concerning the polyhydricity of alcohols by Berthelot, Wurtz, and others also played an important role in questions relating to the formulation of the basic concepts of chemistry, which led to the creation of the theory of chemical structure. Berzelius and his followers already used what they called "rational" formulas, which in their opinion expressed the chemical constitution, understood as the presence in complex substances of separate groups of atoms, i.e., radicals.

Gerhardt, as the leader of the new movement in chemistry, had quite a different view on the significance of rational formulas. Gerhardt understood the rational formulas and constitutions of compounds more in terms of their reactivities than their structures. Gerhardt taught, and was himself firmly convinced, that a chemist can have knowledge of a compound only in the course of chemical reactions, i.e., only when it has ceased to exist as such, and a chemist can therefore know and study only the past and the future of a substance. In accordance with what we have just stated, according to Gerhardt, each substance can be assigned as many rational formulas as there are different types of transformation to which it may be subjected.

On the other hand, the theory of types and the theory of substitution often led their adherents to completely wrong conclusions. Thus, for ethane, as a derivative of the hydrogen type, there was the possibility of two isomers: disubstituted hydrogen — dimethyl, and monosubstituted hydrogen — ethyl hydride, and only by the experimental investigations of Schorlemmer was it shown that dimethyl and ethyl hydride are one and the same compound. However, the arbitrary application of the substitution mechanism later led even some of the most eminent chemists to conclusions that had nothing in common with actuality. In this respect, the activity of one of the first-class German chemists, the brilliant experimentalist H. Kolbe, is of particular significance.

Kolbe was a vehement opponent of Gerhardt's new ideas, and in his theoretical conceptions he reverted in many respects to the old views of Berzelius, rejecting however, the unalterability of radicals in the course of chemical change.

Indeed, Kolbe aimed, in a special sense, at arriving at the chemical "constitutions" of compounds, by which he understood the chemical relations of the separate components and not the disposition of the atoms relative to one another in space; in fact, he constantly expressed doubt whether the determination of the disposition of atoms in space would ever become susceptible to study. The incorrect, though in many respects original, theoretical premises of Kolbe, while leading to some successful predictions concerning the existence of hitherto unknown compounds, led very often also to some quite incorrect conclusions. Using the substitution theory, Kolbe successfully predicted the existence of sec.-propyl alcohol and tert.-butyl alcohol. It should be particularly noted that in interpreting substitution phenomena Kolbe made one additional postulate, viz., that in the course of substitution, the "root radical", i.e., in the simplest case, the carbon atom in the compound, is to be distinguished in some way from the carbon atom entering as substituent, or, as Kolbe expresses it, the former "dominates" over the latter. On this basis Kolbe considered that two isomers were possible for acetone, and he denoted the carbon of the "root radical" by heavy type in the formula. According to Kolbe, one isomer of acetone is doubly methylated carbonic acid, and the other is acetylated methane (Fig. 1). The actual facts, of course, are not in accord with these arbitrary speculations of Kolbe.
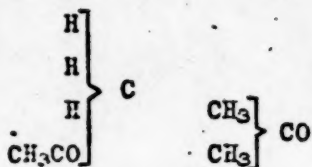
Fig. 1. Kolbe's formula

It should be mentioned here that Butlerov had a high regard both for the experimental and for the theoretical work of Kolbe, and he considered that only misunderstanding and obstinacy in defending his own views prevented Kolbe from associating himself with the new movement in the science. However, the most interesting matter is the position taken up by Kekule on the burning questions of the day. I have already said that we owe to Kekule the establishment of the quadrivalency of the carbon atom and of its ability to form carbon chains. Later, Kekule came to acknowledge the necessity of examining the constitutions of compounds, starting from a consideration of the nature of elements, particularly as expressed by their valency. In this way Kekule moved right up to the problem of the structure of organic compounds, but he did not make the decisive step, which speaks very clearly of his attitude in principle to the problem of structure. At the end of his 1858 article Kekule writes: "In conclusion, I consider it necessary to point out that I myself attribute only secondary importance to considerations of this sort (i.e., considerations concerning structure — A.E.A.). . . .".

Subsequently, Kekule remained for a long time under the sway of Gerhardt's ideas, and in his well known textbook of organic chemistry, published 1859-1861, he makes wide use of "rational" formulas in the manner of Gerhardt. The following examples will serve to confirm this: for acetaldehyde Kekule gives four formulas, for acetone — also four formulas, etc. Only by way of exception does Kekule give a few graphical formulas drawn in very ponderous style. These formulas are given in Fig. 2.

Almost at the same time as the above-mentioned article of Kekule there appeared an article, published in three languages, by the English chemist Couper entitled "A new chemical theory". Couper, independently of Kekule, concluded that investigation into the structures of chemical compounds and into their reactions must start from the concept of the valency of elements.

Assuming valencies of 4 and 2 for carbon, Couper postulates the following two cases:

1) It (i.e., carbon — A.E.A.) unites with the same number of equivalents of hydrogen, chlorine, oxygen, sulfur, etc., which may mutually replace one another, satisfying their combining powers.

2) It (i.e., carbon — A.E.A.) unites with itself. . . . On the basis of these theses Couper, in his article, gives a number of structural formulas as examples; in many ways they are reminiscent of modern structural formulas.

Examples of Couper's formulas are given in Fig. 3.

Acetonitrile   Acetic acid

Fig. 2. Kekule's formulas

In his article Couper gives also a number of incorrect formulas, e.g., those for oxalic acid, glycerol, and others. Couper's scientific activity was suddenly cut short, and he was not able to publish the second article that he had promised on the question of the structure of chemical compounds.

Somewhat later, an article by the German physicist Loschmidt appeared. In this, an enormous number of "constitutional formulas of organic chemistry in graphical representation", based on purely speculative considerations, were given. The spheres of action of the supposed atomic forces were represented by Loschmidt by circles of various diameters. As an example, I am giving a few of Loschmidt's formulas (Fig. 4).
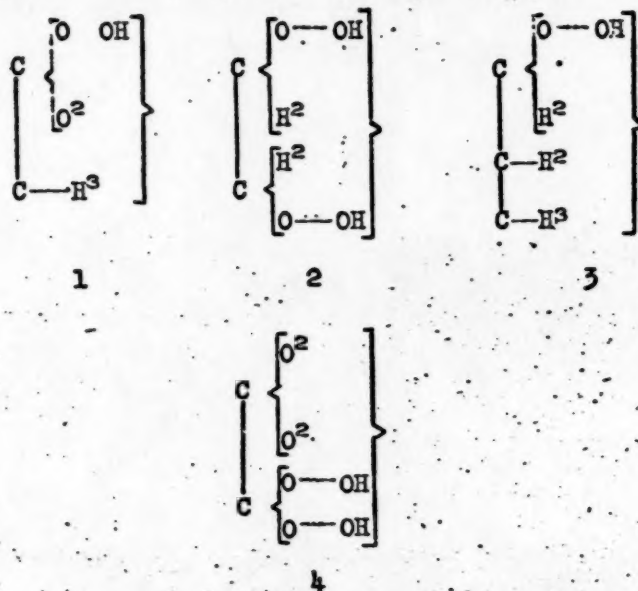
Fig. 3. Couper's formulas: 1) acetic acid; 2) ethylene glycol; 3) n-propyl alcohol; 4) oxalic acid.

Here I wish particularly to state and to emphasize that the purely speculative attempts of Couper and Loschmidt to represent the structures of organic compounds, attempts that were not based on experimental material and not supported by any factual results, passed at the time almost unnoticed and therefore did not and could not influence the course of the development of the problem of the structure of organic or, in the widest sense, chemical compounds.

This, in a few coarse strokes, is my picture of the state of theoretical ideas in chemistry at the end of the sixties and beginning of the seventies of

the last century. There was a feeling that a new phase in the evolution of chemistry was about to begin, but it needed the genius of Butlerov for the Rubicon to be crossed and for science to move forward.
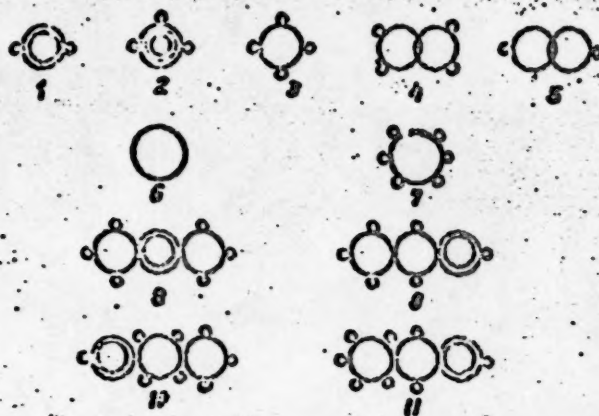
Fig. 4. Loschmidt's formulas: 1) water;
2) ammonia; 3) methane; 4) ethylene;
5) acetylene; 6) benzene nucleus; 7)
benzene; 8) dimethyl ether; 9) ethyl
alcohol; 10) cresol; 11) benzyl alcohol.

It must not be thought, however, that Butlerov found it easy to cross the Rubicon, as I have put it. In 1857, after returning from his first visit abroad, Butlerov gave his students a course in organic chemistry, still following Gerhardt's system, but already in 1859, Butlerov states that "the time has come for us to go beyond Gerhardt". By the end of 1860 Butlerov's theory of chemical structure had fully matured, and he decided to share his ideas with West European chemists.

The paper under the title of "Einiges uber die chemische Structur der Korper" — or translated literally: "Something concerning the chemical structure of bodies" — was read by Butlerov in the chemical section of the 36th congress of German naturalists and physicians on, as we have already stated, September 19th, 1861 at Speyer. This paper is remarkable in that Butlerov, for the first time in the history of chemistry, clearly states the questions at issue concerning the current situation in theoretical chemistry and announces the basic theses of the theory of the structure of organic compounds.

The Russian text of Butlerov's paper, with certain editorial changes, was printed in 1862 in the Scientific Memoirs of Kazan University under the title: "Concerning the chemical structure of substances", it formed an appendix to Butlerov's account of his visit abroad.

Permit me now to dwell on some of the more important points in Butlerov's paper. These consist above all in the definition of the concept of "chemical structure", which Butlerov, in his paper, formulates as follows: "Starting from the idea that every chemical atom that enters into the composition of a body takes part in the formation of the latter and acts there with a definite amount of the chemical force (affinity) that is inherent in it, I give the name of chemical structure to the disposition of these forces, in consequence of which the

chemical atoms, acting directly or indirectly upon one another, unite together to form a chemical particle". This definition of Butlerov is so wide that it does not depart in essence from that which we understand by chemical affinity at the present time, in the light of modern ideas concerning the structure of the atom and of the molecule.

The greatest importance must be attached also to the part of the paper in which Butlerov speaks of the possibility of arriving at the structure of the particles of a substance by chemical methods, particularly by the methods of synthesis of organic compounds.

On this subject Butlerov states in his paper: "Conclusions concerning the chemical structure of substances probably can be based most satisfactorily on a study of the methods of their synthesis, preferably on such syntheses that can be carried out at temperatures not greatly above normal and, in general, under conditions that allow the gradual building up of the complex chemical particle to be followed".

Later in his paper, Butlerov gives 8 rules for the determination of chemical structure. "In the present state of our knowledge," states Butlerov, "the determination of chemical structure can be aided by the following rules, which are deduced from facts and are in part already accepted by the majority of chemists." I shall not go into details and cite these eight rules. However, the most important place in Butlerov's paper is that in which he considers the question of the possibility of expressing the structure of any substance by means of rational formulas.

As I have indicated briefly above, the term "rational formula" has been understood in different ways by various chemists at various stages of the evolution of chemistry. I will again mention that, e.g., Gerhardt and, later, Kekule and many other chemists considered it possible and, in fact, essential to express the structure of one and the same substance by means of several rational formulas. On this question of principle, Butlerov's stand was quite distinct from the views and convictions of all his predecessors. Butlerov, in fact, in contrast to Gerhardt, Kolbe, Kekule, and other chemists, considered it possible and essential to express the structure of a definite compound by means of a single rational formula, i.e., a single structural formula. In his paper, Butlerov defines the content of the term "rational formula" in this way: "If we now make an attempt to determine the chemical structure of substances, and if we succeed in expressing it in our formulas, then these formulas will be approximations, in known measure, to the true rational formulas. In this sense," says Butlerov, "only one rational formula is possible for each substance, and when the general laws relating the chemical properties of substances to their chemical structure become known, then such a formula will be an expression of all these properties."

This is the point in the paper that marks the Rubicon that Butlerov crossed, and it gives us the right to assert that Butlerov is the true creator of the theory of chemical structure. Extremely interesting and significant was the reaction of the majority of the chemists present at the congress to Butlerov's paper, in this, his first great appearance before a wide scientific audience. We may say, in short, that Butlerov's paper was coldly received by the audience. "Of all the chemists of that time," writes Markovnikov on this matter, "only the aged Heinz and the young privatdocent Erlenmeyer took up fully these new ideas and began to apply them in their articles; shortly afterwards, Wislicenus joined them." This state of affairs was very significant: it undoubtedly indicates the state of confusion that reigned in the minds of West European chemists concerning the most fundamental questions of theoretical chemistry.

On his return to Kazan from his visit abroad, Butlerov engaged in intense scientific activity, which was directed simultaneously in two directions — theoretical and experimental. First of all, Butlerov wrote a number of articles in Russian, German, and French, in which he developed his new theory of the structure of organic compounds in greater detail.

Butlerov, being dissatisfied with the development of the theoretical side, came to the conclusion that for the success and recognition of his new theory it was essential to obtain new facts in its support, and with exceptional energy he entered upon wide experimental investigations in the poorly equipped Kazan laboratory. The main result of this period was the celebrated Butlerov synthesis of trimethylcarbinol, the first representative of the class of tertiary alcohols, the existence and structure of which were predicted by Butlerov on the basis of his theory. The preparation by Butlerov of the first representative of an unknown class of tertiary alcohols was of great importance for the recognition and consolidation of the theory of chemical structure.

At this time, at the height of his creative powers, Butlerov prepared his famous textbook "Introduction to a Comprehensive Study of Organic Chemistry" for publication. The first Russian edition of this textbook appeared in 1864 and was completely sold out by 1866. Butlerov then made another very important step — he decided to publish his textbook in German. The German translation was published in Leipzig in 1868.

The publication in Russian and German by Butlerov of his textbook on the study of organic chemistry, a textbook in which, for the first time, the theory of structure was applied successively to all the classes of organic compounds, together with his brilliant researches, of which I have just spoken, changed the attitude of West European chemists to the theory of structure within a very short time.

Butlerov's theory of structure was not only accepted by the great majority of West European chemists, but what is more, Western science, particularly in the person of Kekule, started to dispute Butlerov's priority in the creation of the theory of chemical structure.

However, the little that I have been able to tell you concerning the evolution of the problem of the structure of matter shows without any doubt that not the insecure, inconsistent ideas of Kekule on this subject, nor the abstract notions of Couper and Loschmidt, but the strictly scientific and strictly logical conception of Butlerov was the turning point in the development of the science of chemistry, and I cannot refrain from repeating again that the inception of the new phase in the development of the theoretical basis of organic chemistry was made in Butlerov's paper of September 19, 1861.

It is very surprising that some scientists, only a few, it must be admitted, including even eminent scientists such as the French chemist Berthelot, did not recognize the theory of chemical structure for a long time. As is well known, Berthelot, during practically the whole of his long scientific career, did not acknowledge the reality of atoms, considered it even harmful for the development of chemistry to use the atomic theory, and used only equivalents in his numerous articles. This was Berthelot's position when Mendeleev discovered the periodic law and when, on the basis of this law, hitherto unknown elements were discovered.

It is not less surprising that the creator of the periodic law, Mendeleev, even after the discovery of the law, was critical in his attitude toward Butlerov's theory of structure and preferred to use his own modernized substitution

theory in his organic chemistry course. A more stubborn and consistent opponent of the theory of chemical structure was the well known Russian organic chemist N. A. Menshutkin.

In a series of papers, e.g., in "Phenomena of Isomerism and their Explanation", Menshutkin defended views that were obviously out-of-date, and more than once Butlerov was forced to come forward, in his articles, in defense of his chemical structure theory. Of such articles, that entitled "The Theory of Structure and 'the Theory of Substitution'" was particularly remarkable for its strict exposition and its devastating criticism of Menshutkin's views. This article was published in 1885, a year before Butlerov's untimely death.

I will add that, when in 1898 I attended an organic chemistry course at Zaytsev, the textbook recommended to the students was the latest edition (1896) of Menshutkin's "Lectures on Organic Chemistry". In this edition, the lectures were based on Butlerov's theory of chemical structure, and in several places the significance of structural theory was emphasized. Thus, the last opponent of Butlerov's theory had been overcome.

I would like to conclude my paper by considering briefly what Butlerov's attitude was to the significance of theory and experiment in the realm of experimental sciences. Butlerov was of that rare type of scientist in which the genius of a theoretician is combined with a brilliant experimentalist, and therefore Butlerov's opinion on this matter is particularly valuable.

It seems to me that an almost exhaustive answer to this question was given in an obituary written by Butlerov on the occasion of the death of Academician Fritsche. This is what Butlerov wrote: "In chemistry we are accustomed to attribute the honor of discovery principally to the person who in fact made the discovery, and not to the one who predicted it on the basis of theory. Our theories are still far from perfection; they are born and they die, continually embracing a larger and larger circle of phenomena, but each theory in its time leads to the prediction of new facts -- to discovery. To establish a theory -- this is a great service; to predict a fact on the basis of the existing theory -- this is within the reach of every chemist and may require but a few hours of time; but the factual proof or disproof of such a prediction may require whole months, sometimes years, of physical and mental effort."

A. E. Arbuzov

THE DEVELOPMENT OF ORGANIC CHEMISTRY

IN THE LIGHT OF A. M. BUTLEROV'S TEACHING[1]

Ninety years ago, on September 19, (new style) 1861, at an international congress at Speyer, a young Russian chemist from distant Kazan read a paper on "The Chemical Structure of Substances", in which he expounded his views on the nature of organic compounds, a theory that he called "the theory of the structure of organic compounds". This paper heralded a whole era in the development of organic chemistry. The new approach, which will always be associated with the name of the great Russian chemist Butlerov, resulted in a remarkable development of organic chemistry and of the closely linked organic chemical industry during the whole of the succeeding period. For nearly a century it has been the lodestar that guides investigators on through the fantastic labyrinth of organic compounds. The orderliness of the grandiose system of organic compounds, built on the foundation of a few simple premises, namely, the valency of elements, the ability of carbon atoms to unite together in the form of long chains, and the disposition of atoms in space in accordance with the rules of valency, arouses involuntary surprise and amazement in all who make the acquaintance of organic chemistry.

Only 26 years before Butlerov's theory of structure came into being, Wohler wrote to Berzelius: "Just now, organic chemistry is enough to send a man out of his mind. It has the same effect on me as virgin tropical forest, full of remarkable things and of fantastic unending overgrowth from which it is impossible to extricate oneself and into which it is terrifying to plunge". How has it happened that this fantastic unending overgrowth of the virgin tropical forest of organic compounds has been converted into an orderly system in such a short time?

An enormous amount of experimental material accumulated by organic chemists has been clarified and put into strict order, thanks to the theory of structure. It is difficult to name any other theory that has shown the same ability to make predictions as Butlerov's theory of the structure of organic compounds. Tens and hundreds of thousands of compounds predicted by the theory of structure have been prepared and have served as a brilliant confirmation of the correctness of this theory. The whole of modern organic chemistry with its more than a million compounds is founded on Butlerov's theory of the structure of organic compounds. The work of Butlerov, the founder of the theory of the structure of organic compounds, raised Russian chemical science to an unprecedented level.

Very few scientific generalizations can be named that have turned out to be so fruitful as the theory of the structure of organic compounds. The basic premises of Butlerov's theory of the structure of organic compounds determined the path along which organic chemistry was to develop for a long way ahead. Butlerov's

[1] Paper read at a general meeting of the Division of Chemical Sciences held on September 26, 1951 in celebration of the completion of 90 years since A. M. Butlerov's paper on "The Chemical Structure of Substances."

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theory had a   powerful fruitful influence also on inorganic and on physical chemistry. During the ninety years of its existence, from Butlerov up to our own day, the theory of structure has passed along its complicated evolutionary path. It often appeared that facts did not agree with the theory of structure, that they were in contradiction with it, but this non-accord always turned out to be only apparent and subsequently led only to reinforcement, deepening, and widening of the theory of structure. At first, the theory of structure represented the structure of organic compounds by plane formulas. However, in 1863, i.e., 11 years before the announcements of van't Hoff and le Bel, Butlerov wrote: "If atoms really exist, then I do not see why all our attempts to determine their disposition in space should be in vain, as Kolbe declares it is, and why the future should not be able to teach us how to carry out the required determinations." Thus, Butlerov foresaw the coming of stereochemistry.

Two decades had not passed since the coming of the theory of structure when the theory of the spatial disposition of atoms in the molecule appeared. It came into being as a result of the apparent non-correspondence between the number of isomers predicted on the basis of the premises of the classical theory of structure and the number of isomers actually found. Stereochemistry appeared as an inevitable consequence and development of Butlerov's theory of structure, and it gave invaluable results as regards our knowledge of organic substances, and later also of inorganic compounds. The theory of the asymmetric atom as the source of the optical activity of certain organic substances and the theory of the stereochemistry of unsaturated and cyclic compounds extended our ideas concerning the structure of organic compounds in an extraordinary fashion.

The discovery of optical activity in compounds that do not contain asymmetric atoms, as found in inositol and certain derivatives of biphenyl, gave new material for the study of the geometry of molecules. The theory of the spatial arrangement of atoms in the molecule not only led to the establishment of various types of stereoisomerism, but was extended also to the question of the effect of structure on the reactivity of organic compounds, one of the cardinal questions of organic chemistry, bringing in the concept of steric hindrance in chemical reactions.

The examination of the properties of cyclic compounds from the point of view of a few simplified geometrical concepts, led to the strain theory, which explains to a certain extent the variation in the properties of these organic substances according to the number of members of the ring. However, also in this case the properties of a number of cyclic compounds were not in complete agreement with the theory, e.g. in the case of five- and six-membered rings, and particularly in the case of many-membered rings containing 15-20 atoms in the ring. The discovery of the existence of many-membered rings and of their remarkable stability confirmed the necessity for regarding the disposition of the atoms in the ring not as being in a plane, but in space. All these results show that Butlerov's structural formulas are not the dry immutable schemes that they may appear to be at first glance.

Structural formulas reflect not the statics, but the dynamics of molecules. This is just how Butlerov regarded molecules. "At the present time," writes Butlerov, "we look upon a chemical compound not as   something that is dead and stationary, but we assume, on the contrary, that it is endowed with constant movement, which is present in its very smallest particles, the individual mutual relations of which are undergoing constant changes, which all sum up together, however, as a sort of constant average result." Taking the formation of many-membered rings as our example, it can be shown how an examination of the spatial

disposition of the atoms within the molecule, in their constant state of movement, enables us not only to explain the properties of the molecules, but also to predict the conditions that will be particularly favorable for the formation of such molecules, which are generally prepared with great difficulty.

I should like to point out the principle of high dilution in the synthesis of many-membered rings. The formation of a many-membered ring from molecules that are long and threadlike and have two functional groups at the ends of the chain is not very probable because there is a low probability of the ends of the chain coming sufficiently close together in the course of the movements of the threadlike molecule for the closure of the ring to become possible. The meeting of the functional groups of different molecules, which would lead to the formation of linear polymers, is much more probable. By diluting the initial bifunctional compound with an inert solvent, it is possible to reduce the probability of encounters between functional groups of different molecules and increase the probability of an approach to within a short distance of the functional groups of one and the same molecule, thus increasing the probability of the closing of the many-membered ring. By applying this principle of high dilution; taking, for example, 1.5 g of initial substance and diluting with 9 liters of solvent, it is possible to obtain high yields of the many-membered ring.

I think that these examples show quite clearly that Butlerov's theory of the structure of organic compounds, enriched by spatial concepts, correctly portrays the kinetic condition of the molecules. The extension of inferences from the theory of structure and from stereochemical concepts to inorganic compounds has undoubtedly had a great influence on the emergence and development of coordination theory. At the basis of Butlerov's teaching lies the concept of the linkage of atoms in the molecule in accordance with valency rules.

For carbon, the essential element of organic substances, chemists came to recognize, after some vacillation, a constant valency of four. The exception was carbon monoxide. However, it was later necessary to acknowledge the presence of bivalent carbon in whole classes of organic compounds: the isonitriles and derivatives of fulminic acid. In 1900, the possibility of the existence of tervalent carbon was discovered for the first time, the example being triphenylmethyl; later the existence in other elements of abnormal valency was discovered. Free radicals containing tervalent carbon and bi- and quadri-valent nitrogen were prepared only in the case of heavy aromatic radicals.

All attempts at preparing free radicals of the aliphatic series were invariably unsuccessful, but in 1929 the free radical methyl was prepared and the possibility of the existence of simple aliphatic radicals was thus demonstrated. Also, the reason for previous lack of success became understandable. The life of the free methyl radical turned out to be very short, the half-life being only 0.006 sec. Organic chemistry was enriched by an interesting peculiar group of compounds. At first it seemed that this group of organic compounds would be very much circumscribed with respect to the conditions of their formation and existence. However, the further development of this branch of organic chemistry has shown the reverse.

It has been found that the simple free radicals derived from tervalent carbon are formed in a number of processes that are important both from the theoretical and the practical points of view, and that they play an essential role in these reactions. Free radicals play an important part in the pyrogenetic decomposition of organic substances in the cracking process. A prominent role is to be attributed to free radicals in various polymerization processes that yield products of great practical importance. Free radicals play an essential part in

photochemical processes, the reactions of diazo compounds, catalytic halogenation, and many other processes. Free radicals, the existence of which seemed to be so improbable when triphenylmethyl was discovered, since they did not conform to the concepts of the theory of structure, later resulted in development and enrichment of this theory.

In considering the development of organic chemistry during the time from the inception of the theory up to the present time, it is impossible not to take note of the progress that has been made in these 90 years in the study of macromolecular compounds, both natural and synthetic. The chemistry of macromolecular compounds began to develop considerably later, which is quite understandable if the difficulties that are met in their study are taken into consideration. Macromolecular compounds were at first regarded as being made up of small highly associated cells, and colloidal solutions of macromolecular compounds as consisting of colloidal particles of micellar structure. It therefore appeared that the theory of structure of organic compounds did not have the same significance in this sphere as it has for low-molecular-weight compounds. It appeared that for the majority of macromolecular compounds the question of the elucidation of their structure and the structure of their colloidal solutions was a problem rather for colloid chemistry than for organic chemistry. Nevertheless, this turned out to be incorrect, and for the majority of typical macromolecular compounds, both natural and synthetic, the application of the theory of structure has been found to be correct and fruitful.

It is now quite obvious that the gigantic molecules of macromolecular compounds are true molecules. Thousands of carbon atoms may be united one to another forming long threadlike molecules or fantastic three-dimensional network structures. Organic chemistry has been enriched by a new sphere of colossal theoretical and practical significance — the chemistry of macromolecular compounds, while the theory of structure has been enriched by new ideas and concepts, such as the concept of polymer-homologous series, etc.

In considering the development of organic chemistry it is impossible not to take note, even if only very briefly, of the achievements in the study of natural substances that play an enormous part in the life processes of animal and vegetable organisms. While at the end of the last century and the beginning of the present century fundamental investigations were made into the nature of compounds found in nature in large amounts, the last 20-30 years has been characterized by great success in the study of compounds that are formed in living organisms in negligible amount and yet play an important part in their life processes. I am thinking of the progress made in our knowledge of the nature of vitamins, hormones, and antibiotics.

The characteristic peculiarity of these investigations has been processes in which we pass from hugh quantities of initial materials, often expressed in thousands of kilograms, on to insignificant amounts of end products, expressed in grams, or sometimes in tenths, hundredths, or even thousandths of a gram. Thanks to the development of micro-analysis and of methods of dealing with very small amounts of material, it became possible to establish the structures of complex substances, in spite of the fact that they were available in quantities that would at one time not have sufficed for a single elementary analysis.

It should be noted that, while on the one hand organic chemistry has given medicine a powerful weapon in its fight against disease, in the form of various medicinal preparations, and has helped to some extent to elucidate the nature of the processes that accompany various departures from normal functioning in an organism, on the other hand the demands of practice have stimulated investigations in particular branches of organic chemistry, leading to their rapid devel-

opment. Thus we have the example of the influence exerted by the problem of experimental cancer on the development of the chemistry of polynuclear compounds of aromatic character; also, the influence of the study of the nature of the sex hormones on the chemistry of the hydrogenated derivatives of phenanthrene and related substances.

Study of the nature of vitamins and the problem of their synthesis led to intensified development in certain sections of the chemistry of heterocyclic compounds. Sometimes, as in the case of sulfamide preparations, many thousands of new compounds were synthesized with the result that perhaps ten might be applied widely in medical practice. All this progress in organic chemistry became possible only on the basis of Butlerov's theory of structure.

Placed at the basis of Butlerov's theory of the structure of organic compounds is the idea that "the chemical nature of a complex molecule is determined by the nature and number of its elementary component parts and by its chemical structure". Chemical structure is often erroneously regarded as merely the relative disposition of the atoms in the molecule, which are united together in accordance with the rules of valency. Butlerov's views on the structure of an organic molecule were wider and deeper than this.

Already in his paper at the international congress at Speyer in 1861 Butlerov states that atoms, by directly or indirectly acting upon one another, are linked together to form the chemical particle — the molecule. This idea of the mutual interaction of atoms in a molecule, whether they be directly united one to another or not, was frequently expressed by Butlerov. This idea of Butlerov was more fully developed later by his eminent pupil and follower Markovnikov. In his famous dissertation, "The Mutual Effects of Atoms in Chemical Compounds" (1869), Markovnikov wrote: "The question of the effect of elementary atoms on the course of the chemical reactions of a complex body is one of the most thrilling questions of modern chemistry and, as is already noticeable, is occupying more and more of the attention of chemists". This question of the interaction of atoms in the molecule of an organic substance and of the effect of the structure on the reactivity of the molecule is still one of the most thrilling and vital questions of present-day organic chemistry.

Neither Butlerov nor Markovnikov were in a position to explain the mechanism of the transmission of mutual effects of atoms in the molecule. They could not explain what was hidden behind the line that was used to indicate the linking together of atoms in the molecule. Naturally, the state of knowledge at that time was such that it would have been difficult to demand an answer to this sort of question from the theory of structure.

Also, the separate chemical bonds in the structural formulas were not all identical to the organic chemist, in spite of being denoted in all cases by the same sign — a line.

The formal language of structural theory — a line to indicate a single bond between atoms, or lines to indicate double or triple bonds — is too meager for the expression of all the variety in chemical behavior of the various atoms and groups of atoms in the molecule of an organic substance. This diversity in chemical behavior of atoms or groups of atoms is associated by the organic chemist with the general structure of the molecule and is an expression of the rich experimental material accumulated by organic chemistry, and it certainly cannot be directly represented by a line, as such.

Organic chemists have long felt the inadequacy of the language of classical structural theory, and this has led to the emergence of supplementary hypotheses

of oscillating valencies, partial valencies, etc. Nevertheless, these supplementary hypotheses also were unable to explain satisfactorily the experimental results that were being yielded by the rapidly expanding organic chemistry. By way of example, we may point to the disillusionment of Thiele regarding his theory of partial valencies and to the pessimistic conclusions of Wislicenus, when he surveyed his life-work on tautomerism. This rich experimental material has been brought together by organic chemists in the form of so-called rules. In this way there arose the rules of Markovnikov, Eltekov, Zaytsev, Popov, etc.

However, in spite of the imperfections of the language of structural theory, organic chemists, by applying this theory, succeeded in correctly establishing the structures of extremely complex organic compounds. They succeeded in establishing the structure correctly even when the reactions used as a means of establishing the structure went in an abnormal fashion and were accompanied by a rearrangement, sometimes a far-reaching rearrangement of the skeleton of the molecule, i.e. the type of reaction that is accompanied by all sorts of isomerizations and regroupings. Among the investigations of this sort are the classical researches of Butlerov's pupil Vagner in the terpene field, the work of Demyanov on the isomerization of rings, and many others. These instances, which at first glance did not seem to agree with inferences from the theory of structure, later served only to strengthen and extend it.

Since the time of Butlerov's paper at Speyer, 90 years have passed. During this period there have been some very great discoveries contributing to our knowledge of matter. The atom has turned out to be a complex system. Our concept of the nature of the chemical bond has been changed and deepened. Our ideas concerning the structure of organic molecules and of the mechanism of chemical processes have been extended and enriched. All this progress and these new ideas were bound to be reflected in the theory of the structure of organic compounds. The development of our knowledge concerning the structure of the atom made it necessary to link these ideas with the classical theory of structure, and this was done Gradually electronic concepts penetrated more and more into organic chemistry. At first, the electronic formulas were merely restatements of the classical structural formulas in electronic language. Later, electronic ideas were able to explain the non-equivalence of the various covalent bonds, which is the result of mutual effects of atoms or groups within the molecule. The basis of these ideas was the concept of electronic displacements, brought about by internal and external causes. The concept of electronic displacements, characteristic of the state of polarization or the polarizability of the molecules, i.e. the distribution of electron density in the molecule, enabled a clearer picture to be formed of the mutual effects of atoms in molecules and of the transmission of these effects. To a certain extent it gave an explanation for the peculiarities in behavior of conjugated systems of double bonds and of aromatic and other compounds, and it led to the discovery of the phenomenon of vinylogy.

Concepts concerning the variation in electron density in various parts of a molecule, due to internal or external causes, enabled a clear picture to be formed of the basis of the rules of Markovnikov and Eltekov concerning the orienting effects of substituents in the benzene nucleus. On the basis of ideas concerning the electron density in a molecule, concepts were worked out relating to the electron-donating (nucleophilic) and electron-accepting (electrophilic) characters of reagents. These concepts constitute a step forward in the development of Butlerov's theory of structure, in the theory of the mutual effects of atoms in a molecule, and in the theory of the relation between molecular structure and reactivity. These concepts, however, are far from perfect. They permit only a qualitative explanation of the mutual effects of atoms linked together in a

molecule. The method of representing electron density distribution is imperfect. It has many deficiencies, the main one being that, with this method of representation, the state of a molecule of an organic compound can be interpreted both from the point of view of the materialistic theory of Butlerov and also in the spirit of the idealistic teaching of the so-called "theory of resonance".

At first the concept of electron displacements was directed towards the interpretation of experimental data concerning the effects of atoms or groups of atoms forming part of the molecule on the behavior of the molecule as a whole. Later, however, the most prominent representative of this school, the English chemist Ingold, went over to the erroneous idealistic concept of electronic resonance.

A fundamental part in the development of our concepts concerning the nature of chemical affinity and of the structure of organic molecules has been played by the application to chemistry of quantum mechanics. Quantum chemistry has enabled new concepts concerning the nature of the chemical bond to be formed.

The application of quantum mechanics to questions in the theory of structure has enabled a physical basis to be given to some of the fundamental premises of this theory. Quantum chemistry has given an explanation of the nature of the capacity for saturation in a chemical bond, of the tetrahedral configuration of the carbon atom in saturated compounds, and of the characteristics of multiple bonds. Certain predictions of quantum chemistry have received experimental confirmation, as, for example, the effect of co-planarity on the properties of molecules containing conjugated bonds.

The field of applicability of quantum-mechanical calculations, however, is limited to only the very simplest molecules; quantum-mechanical calculations on polyatomic molecules are extremely approximate, and quantitative results obtained by their aid are not reliable. Hence, these calculations permit only general qualitative inferences that may permit some of the peculiarities of complex molecules to be interpreted. The progress that I have indicated in the development of our concepts concerning the nature of organic molecules and the course of the chemical changes of these molecules is based on the further development and deepening of Butlerov's teaching.

In the last 10-15 years, attempts have been made to revise the principles of Butlerov's theory of structure, as if it were not able to explain the properties of organic compounds and, to represent correctly the nature of the processes determing the course of chemical reactions. These attempts come from the adherents of the "theory of resonance", which is bound, in the opinion of those adherents, to replace Butlerov's theory of structure. This "theory" lays claim to a leading role in organic, physical, and inorganic chemistry, to the role of a universal theory that has its source directly in the concepts of contemporary quantum mechanics. This theory has received wide acceptance among foreign chemists and also within a certain section of Soviet chemists.

During the last 2-3 years, the "theory of resonance" has been subjected to detailed analysis and justifiable criticism in a series of discussions and conferences, and in our journals. These discussions have made abundantly clear the erroneous and idealistic nature of this "theory" and the harm that it has done to the development of the theory of chemical structure, diverting workers from the true path and creating the harmful illusion of explaining observed facts, which, in fact, remain unexplained.

In describing the development of the theory of the structure of organic compounds, I consider it essential to point out the part played by physical and physico-chemical methods in the study of the structure of organic compounds. Physi-

cal methods of investigating the structure of organic compounds have given and are still giving invaluable help in the task of determining the nature of organic substances. Spectroscopic, electronographic, and X-ray analysis methods, and also the method of dipole moment determination, have enabled all the fundamental parameters of organic molecules to be determined. They have permitted us to determine the configurations of the atoms linked together in the molecule, to estimate the valency angles, to determine the interatomic distances within hundredths of an Angstrom, and to find the distribution of electron density in various parts of the molecule. Magnetic methods of investigation are the best for the detection of free radicals.

.Physical methods are of very great importance in the study of macromolecular compounds and of catalytic and many other processes. Physical methods of investigating the structure of organic compounds have confirmed the postulates on which the theory of structure is based and have furnished weighty evidence for the correctness of the theory. The structure of the molecules of organic compounds – the concept that lies at the basis of Butlerov's ideas – is an actual reality. We are not only certain that the atoms are united one to another in accordance with the laws of valency, as follows from Butlerov's theory of structure, but we can measure the distances between these atoms to an accuracy of a few millionths of a millimeter.

By the aid of a beam of electrons we may almost photograph the molecules of organic compounds. The pictures obtained of the structures of the most complex organic molecules, such, for example, as the phthalocyanines, by analysis of their electronograms coincide exactly with the structural formulas derived on the basis of Butlerov's classical theory of structure. By way of example we will consider platinum phthalocyanine.

On Figure 1 is shown the structural formula of platinum phthalocyanine constructed in accordance with Butlerov's theory. On Figure 2 is shown the electronogram of the same compound.

In order to make the striking correspondence between the structural formula of platinum phthalocyanine and its electronogram still clearer, the structural formula of the phthalocyanine has been superimposed on the electronogram in Figure 3.

Ninety years have passed since the theory of structure was created, and it still remains the basis of modern organic chemistry and for yet a long time to come will remain the foundation of our knowledge of organic substances. For almost a century the theory of structure has been the guiding thread for organic chemistry. Few scientific generalizations could be named that have stood firm for so long a time.

What then is the reason for the great importance of the theory of structure?

It is that at the basis of the immense importance of Butlerov's theory of structure and of its immutable nature lies a true portrayal in its materialistic character of the actual real world. The correctness of the theory of structure has been verified countless times and is being verified in practice at present. This verification has been done and is being done both in laboratories and also in industry, in the manufacture of organic substances on an immense scale in the factories. Right up to the present time, Butlerov's theory of structure continues to give organic chemistry a powerful stimulus to further development.

Nevertheless, however great may be the progress of organic chemistry, and however great may be the importance of the theory of structure, we must still remember the remarkable words of its founder Butlerov when, in considering the
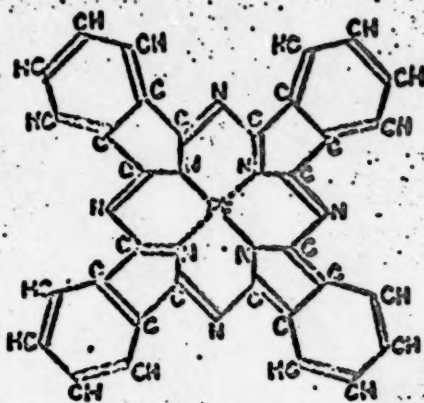
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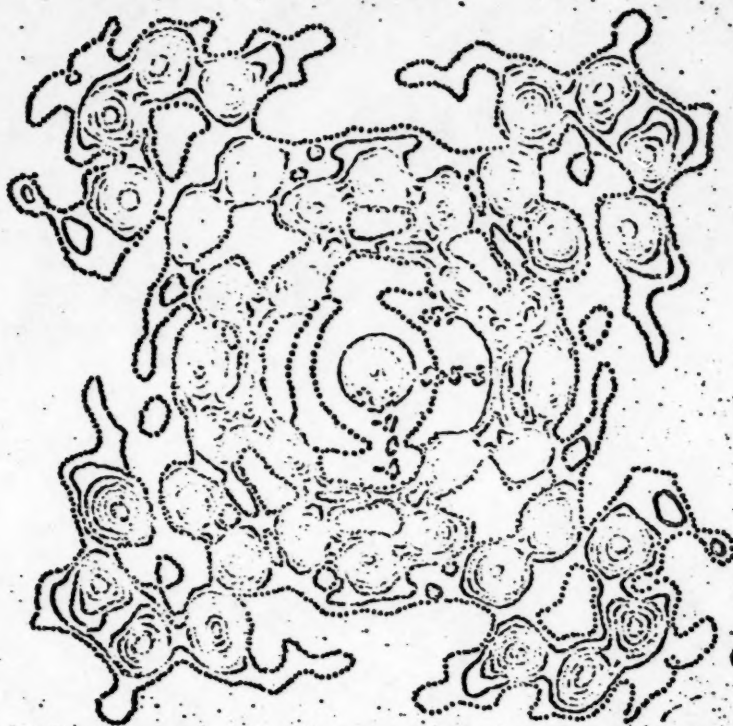
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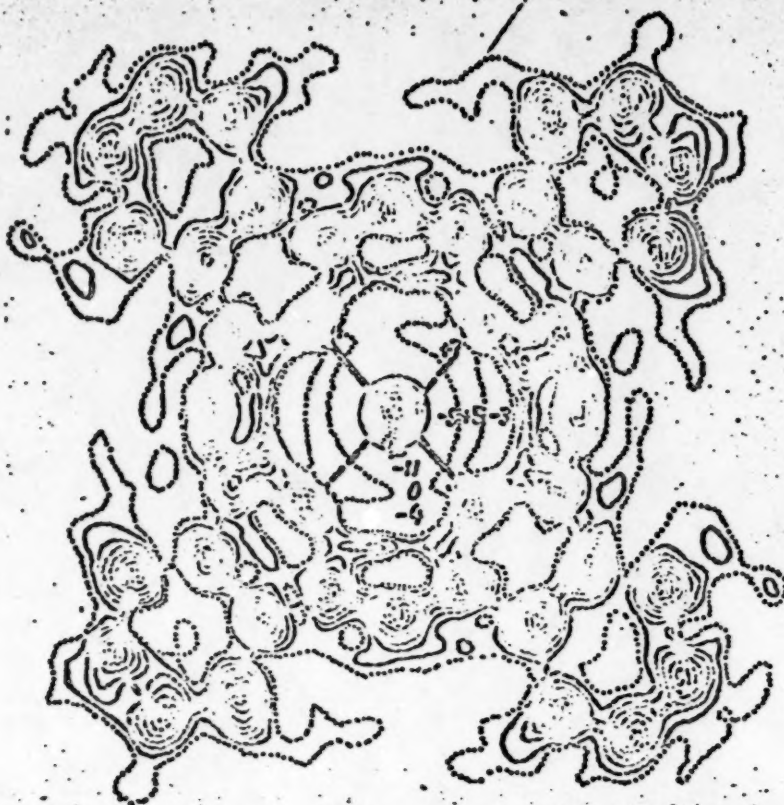
Fig. 3.

role of theory in scientific investigations, he wrote: "Only through the medium of theory does knowledge, by being brought together to form a connected whole, become scientific knowledge; the orderly coordination of knowledge constitutes science. But however perfect a theory may be, it is still only an approximation to the truth."

Before us, as Soviet chemists, there lies a great and noble task: to extend and deepen in creative fashion the teaching of the great Russian chemist Butlerov. We must study the wealth of material that Butlerov has left to us in his works. The further development of A. M. Butlerov's theory of structure will guide the organic chemistry of our country to a yet fuller blossoming worthy of the great era in which we live — the era of the building of communism.

                                                        B. A. Arbuzov

PHENOL COMPOUNDS OF THE INERT GASES AND THEIR ANALOGS

B. A. Nikitin and M. P. Kovalskaya

In previous investigations it has been shown that the inert gases, as well as giving the already known hydrates, give also compounds with phenol and toluene [1]. At the same time it was established that in their formation of molecular compounds the inert gases have numerous analogs among the volatile hydrides and also, in the case of the hydrates, among substances whose molecules contain many atoms. This analogy is shown above all in the similarity of the conditions of formation and, particularly, in their isomorphism. Foreign workers [2] have established the formula $H_2S \cdot 2C_6H_5OH$ for the compound of hydrogen sulfide and phenol, using fusion diagrams. Nikitin [3] showed that the inert gases are isomorphously co-precipitated with the H_2S — phenol compound, and he concluded that the inert gases form analogous compounds, to which he ascribed the same type of formula. Later, he prepared directly compounds of xenon and krypton with phenol [4], but the thermal analysis of the H_2S — phenol system was done only from the liquidus curve and without taking into account the amount of hydrogen sulfide remaining in the gas phase. By the use of a specially developed method for the thermal analysis of systems containing a volatile component, Nikitin, Kovalskaya, and Pushlenkov [5] carried out a more accurate determination of the fusion diagram for this system and showed that the compound must be assigned the formula $H_2S \cdot 3C_6H_5OH$.

A question of great interest for the further development of the chemistry of the inert gases is the determination of what substances behave in analogous fashion with respect to the formation of compounds with phenol. As the hydrates of the inert gases not only have an analogous formula to the hexahydrate of SO_2, but are also isomorphous with it [6], we decided to examine whether this analogy is shown also in the compounds with phenol, using radon as our example. If radon is taken up from the gas phase by crystals of the SO_2 — phenol compound and this capture proceeds according to Khlopin's isomorphous co-precipitation law, then both the isomorphism and the analogy in formula will be shown for these compounds [1]. The investigational method was the same as that used in the study of the co-precipitation of radon with crystals of the H_2S — phenol compound [3]. Finely ground, carefully dried phenol was introduced into a U-tube having a ground joint and two taps. The volume of the gas phase was then measured, and a definite amount of SO_2 was introduced into the reaction tube. A compound was formed from the gaseous SO_2 and the solid phenol, the temperature being below that of the eutectic. In one series of experiments, some radon was first admixed with the sulfur dioxide, and under these conditions the crystals of the compound took up radon at the moment of their formation. The tube was then allowed to stand for a long time to permit the attainment of equilibrium in the distribution of radon between the gas phase and the crystals of the compound (Method I).

In another series of experiments, the compound was formed in absence of radon, which was then introduced into the reaction tube. By carrying out the complete recrystallization of the compound, uptake of radon was promoted and a state of equilibrium in its distribution between the gas phase and the crystals of the SO_2 compound was attained (Method II). The amount of radon taken in each

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experiment was about 10^{-12} g. Knowing the dissociation pressure of the SO_2 compound, the volume of the gas phase, and the amount of SO_2 taken for the experiment, it is easy to calculate the amount of SO_2 in the gas and in the solid phase. At the end of the experiment, the tube was cleared by means of a stream of air containing sulfur dioxide in such amount that its partial pressure corresponded to the dissociation pressure of the compound at the given temperature. This prevented decomposition of the compound during the clearing. The radon was determined radiometrically both in the gas phase and in the air-swept crystals. If repeated recrystallization of the compounds of SO_2 (the macro-component) has resulted in the establishment of equilibrium in the distribution of radon (the micro-component) between the gas and solid phases, then the distribution must be in accord with Khlopin's law:

$$\frac{\% Rn \text{ in cryst. phase}}{\% Rn \text{ in gas phase}} = D \frac{\% SO_2 \text{ in cryst. phase}}{\% SO_2 \text{ in gas phase}}$$

where D is a constant at a given temperature. The experiments were carried out at 0°. The results are given in Table 1.

TABLE 1

Method	Duration of recrystallization in hours	% SO_2 in crystals	% Rn in crystals	D
I	72	77.2	45.4	0.25
II	120	80.0	54.7	0.30
I	67	89.8	75.7	0.35
II	120	90.3	71.0	0.26
I	24	96.5	88.9	0.30
II	73	97.1	92.1	0.35
I	24	97.6	92.9	0.32
II	74	98.0	93.9	0.31
			Mean	0.30±0.03

From this table it will be seen that radon is readily taken up by crystals of the compound of SO_2 with phenol and that the capture proceeds according to the amorphous co-precipitation law, for the distribution constant D remains, in fact, constant within limits of experimental error (about ± 10%); at 15°, D = 0.24.

According to the isomorphous co-precipitation law, the compound of Rn with phenol should have a formula that is analogous to that of the SO_2 – phenol compound. For the compound of H_2S with phenol we have already established the formula $H_2S \cdot 3C_6H_5OH$ and have shown that radon is isomorphously co-precipitated with it (at +15°, D = 1.25). However, the compound of SO_2 with phenol has hitherto been assigned another formula. It was first prepared by Meyer and Kolbe (8) already in 1881. On the basis of the results of the analysis of the compound they assigned it the formula: $SO_2 \cdot 4C_6H_5OH$ or $SO_2 \cdot 5C_6H_5OH$. Since the compound dissociates appreciably in the air with loss of sulfur dioxide and the authors took no precautions during the analysis, their proposed formulas do not appear very convincing.

We decided to determine the formula of this compound by means of thermal analysis, using the procedure we had worked out earlier for analogous systems [5]. As the system contains a volatile component, it was necessary first to determine the temperature – pressure diagram when the system contains three phases – solid, liquid, and gas – in equilibrium. This is required to enable a correction to be made for the amount of sulfur dioxide remaining in the gas phase when calculating the molecular ratio of components in the course of constructing the fusion diagram.
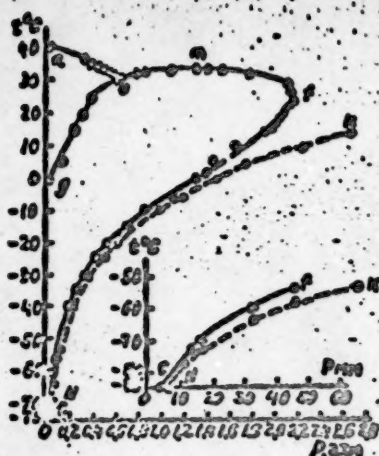
Fig. 1. Temperature – pressure diagram for the system SO_2 – C_6H_5OH
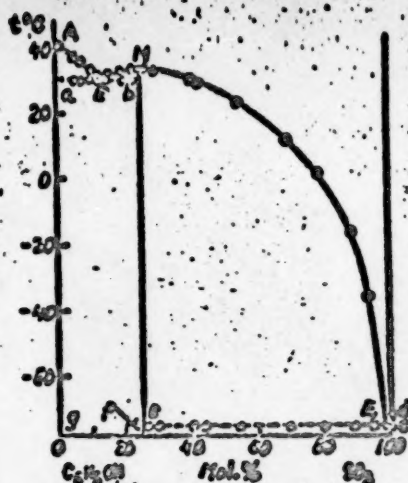
Fig. 2. Fusion diagram for the system SO_2 – C_6H_5OH

The phenol used in these investigations melted at 41.0° and boiled at 180°. According to analysis, the sulfur dioxide contained less than 0.5% impurity. A weighed amount of carefully dried phenol was introduced into a glass tube made from barometer tubing and having a capacity of 2-3 ml. The tube was fused to a glass mercury manometer graduated up to 10 atm. The air was then pumped out of the apparatus, the tube was cooled in liquid air, and from an attached buret a definite amount of sulfur dioxide was introduced. The tube through which the sulfur dioxide was introduced was then sealed off so that the apparatus was now hermetically sealed. In the tube containing the substance there was a small electromagnetic stirrer, which was placed there beforehand.

In order to determine the equilibrium pressure, the tube containing the substance was maintained at a definite temperature in a cryostat or thermostat, and the liquid was vigorously stirred with the electromagnetic stirrer. The results obtained are shown graphically in Fig. 1. The curve ae on this diagram shows the dependence of pressure on temperature when gaseous SO_2, the melt, and solid phenol are in equilibrium. Point e corresponds to the eutectic point. The curve emfN relates to the case where the solid phase is a compound. It is already evident from this diagram that a compound is formed in the system with a melting point of 34.2°. For comparison, the curve NK has been inserted in the diagram; it shows the variation of the vapor pressure of pure SO_2 with temperature. Curve ge shows the dissociation pressure for the conversion of the solid compound into solid phenol and gaseous sulfur dioxide.

It was found impossible to determine the fusion diagram by the method of temperature halts because a great deal of supercooling is observed in the SO_2 – phenol system. Hence, we determined the liquidus curve visually by noting the temperature at which the last crystal disappeared, the liquid being constantly stirred. We determined the solidus curve by centrifuging sealed tubes at temperatures as close as possible to the eutectic temperature, following the method already developed. A piece of barometer tubing blown out at the fused end served as reaction vessel. At the other end of the tube there was a ground joint, and through this joint a definite weight of phenol was introduced, and the electromagnetic stirrer was inserted. A glass vacuum tap was then inserted into the joint, and the air was pumped out of the tube. The blown-out end of the tube,

which contained the phenol, was then immersed in liquid air, and from a buret a definite amount of sulfur dioxide was introduced through the tap. The tube was then fused off below the joint. In the determination of the liquidus curve, the tube containing the substance was first warmed until the latter was completely melted, and it was then immersed in liquid air. From there it was removed, depending on the temperature of fusion, into a transparent cryostat or thermostat, in which the temperature was raised slowly (at 2-3° per hour). At the same time the liquid was stirred with the electromagnetic stirrer. Two eutectic points were found on the liquidus curve: 31.5° (13 mol.% SO_2) and -75° (98.8 mol. SO_2). For the determination of the solidus curve, the same tubes that were used for the determination of the liquidus curve were again cooled in liquid air. They were then allowed to stand at close to the eutectic temperatures and were centrifuged at these temperatures. For this purpose, the tubes were immersed, capillary end downwards, in a cup of the centrifuge that was filled with crystallizing guaiacol (29°) or melting chloroform (-63°). After centrifuging for 3 min. at 3000 rev. per min., the tubes were taken out of the cups, and the presence or absence of liquid in the capillary was determined visually. The tube was then opened and its capacity determined. The volumes of the stirrer and of the liquid and solid phases were subtracted from the value obtained, thus giving the volume of the gas phase. The amount of sulfur dioxide remaining in the gas phase was calculated from the pressure — temperature diagram, and this was subtracted from the amount of SO_2 taken for the experiment. As the maximum pressure in the system did not exceed 2.2 atm. and the dead space was not more than 1 ml, the correction was not greater than 2.5%. 0.5-0.01 g phenol and 5-200 ml SO_2 were taken for the experiment.

It must be noted that, owing to the variation of the pressure of SO_2 with temperature, for a given tube the points on the liquidus and on the solidus curve corresponded to different molecular percentages of SO_2. The results obtained are shown in Table 2 and on Fig. 2. At 29°, samples No. 2 - 8 showed no trace of liquid. On allowing them to stand in a thermostat (at 32°) with their capillary ends downwards, liquid could be seen running down the capillary. This crystallized with supercooling, but in all cases the crystals formed largely melted at 31.5°, since they consisted of almost pure eutectic mixture. In sample No. 9, liquid could be observed at 33.5°.

On centrifuging tubes No. 10 - 20 in melting chloroform (-63°), liquid appeared in the capillary in all cases. After the complete crystallization of this liquid at lower temperatures, the commencement of fusion of the crystals formed was observed in all cases at -75°. It follows from all these results that the line denoting the composition of the compound must be drawn at 25 mol.% SO_2, and that the compound must be assigned the formula $SO_2 \cdot 3C_6H_5OH$.

As the pressures in the system SO_2 — phenol turned out to be low, we decided to make an attempt to analyze the compound also chemically. For this purpose, a weighed amount of phenol was introduced into a U-tube having a joint and two taps. The air was then pumped out of the tube, and sulfur dioxide was introduced into the tube at -15° in amount sufficient to dissolve the phenol completely. The tube was then cooled until crystals of the compound made their appearance. The greater part of the sulfur dioxide was then removed by pumping. A manometer was attached, and pumping was continued at 0° until the pressure fell to 72 mm (the dissociation pressure of the compound [giving solid phenol and gaseous SO_2] at 0°). The crystals should now constitute a pure compound. The amount of SO_2 remaining in the gas phase was taken into account. NaOH solution was then introduced into the tube, so that the compound was completely decomposed. This procedure fully ensured that SO_2 would not be lost, but it did not preclude the possibility that

TABLE 2

No. of tube	Mol.% SO_2	Temperature at end of fusion (°C)	No. of tube	Mol.% SO_2	Temperature at beginning of fusion (°C)
1	0.00	41.0			
2	4.74	37.6	2	4.59	31.5
3	6.88	36.4	3	6.81	31.5
4	9.73	33.9	4	9.73	31.5
5	10.02	32.4	5	10.02	31.5
6	14.79	32.6	6	14.89	31.5
7	19.52	33.8	7	19.63	31.5
8	22.79	34.2	8	22.90	31.5
9	24.85	34.2	9	24.85	33.5
10	26.34	34.1	10	26.98	−75.0
11	29.49	33.9	11	29.80	−75.0
12	40.73	31.4	12	41.28	−75.0
13	42.91	30.0	13	43.43	−75.0
14	54.24	24.4	14	54.68	−75.0
15	69.74	13.2	15	69.98	−75.0
16	79.42	3.4	16	79.51	−75.0
17	89.50	−15.0	17	89.61	−75.0
18	95.02	−35.0	18	95.02	−75.0
19	98.79	−75.0	19	98.79	−75.0
20	98.94	−74.0	20	98.94	−75.0
21	100.00	−73.0	21	100.0	−73.0

mother liquor would be retained by the crystals and might therefore give high values for the amount of SO_2. The sulfur dioxide was oxidized with hydrogen peroxide, and the sulfate ions formed were precipitated with barium chloride. The following results were obtained in this way:

To each mol. SO_2 — 2.86; 2.79; 2.90; 2.86 mol, C_6H_5OH.
Mean: 2.87 mol. C_6H_5OH per mol. SO_2.

Hence, the results of thermal and of chemical analysis are in good agreement. This shows that the compound has the formula $SO_2 \cdot 3C_6H_5OH$, analogous to the formula of the compound of H_2S with phenol.

Nikitin [4] has previously prepared a compound of HCl with phenol and has shown its isomorphism with the xenon-phenol compound by tensimetric analysis. We decided to try to determine the formula of the compound of HCl with phenol. This compound melts congruently at 35.9°. The part of the fusion diagram that we have determined in the region close to the composition of the compound shows a maximum on the liquidus curve at 27.5 mol.% HCl. However, we did not determine the pressure – temperature diagram and could not therefore take into account the amount of HCl remaining in the gas phase. Consequently, the true composition of the compound must correspond to a somewhat lower content of HCl. It is most probable that this compound has also the formula $HCl \cdot 3C_6H_5OH$. The chemical analysis of this compound, obtained by crystallization from melts greatly enriched in HCl at −100° and by then removing excess HCl at this temperature by pumping, showed 29 mol.% HCl. Hence, this method of establishing the formula of the compound is very approximate, since it gives no guarantee that excess of a component will not be retained, particularly when the compound is prepared at very low temperatures.

In order to show the analogies existing among substances that form compounds with phenol, it is of great interest to determine the heats of formation of these compounds from the gas and solid phenol. Having determined the dissociation pressures at various temperatures below the eutectic point, the heats of formation may be calculated by Clapeyron's formula:

$$Q = -R \cdot 2.303 \frac{d \log p}{d 1/T}$$

where Q is the heat of formation in kcal per mole; R is the gas constant; p is the dissociation pressure; and T is the absolute temperature. The dissociation pressures of various compounds determined by us earlier [1] or in the present work are given in mm Hg in Table 3.

TABLE 3

Gas	Dissociation pressure of the gas in mm Hg at temperature:							
	-30°	-20°	-10°	0°	5°	15°	20°	25°
CO_2	240	437	770	1340	——	——	——	——
Xe	115	195	330	630	——	——	——	——
HCl	106	187	319	560	——	——	——	——
H_2S	35	60	108	198	——	449	580	750
HBr	29	50	91	160	——	362	475	621
SO_2	——	——	——	72	100	179	238	323

Forcrand [9] calculated the heats of formation of hydrates of gases by a modified Trouton formula: $Q = 30T$, where T is the absolute temperature at which the dissociation pressure reaches 1 atm.

In Table 4 we give the melting points of these compounds and the temperatures at which $p = 1$ atm; there follows the heats of formation, calculated according to Clapeyron and to Forcrand, and also the heats of formation of the corresponding hydrates, calculated by Forcrand.

TABLE 4

Gas	Temperature in °C		Heat of formation in kcal		Hydrates, acc. to Forcrand
			Compounds with phenol		
	of melting	at which P = 1 atm.	Acc. to Clapeyron	Acc. to Forcrand	
CO_2	45.4	-10.3	7.32	7.89	7.55
Xe	-	4.0	7.33	8.31	8.16
HCl	35.9	5.8	7.38	8.37	-
H_2S	47.4	25.3	8.45	8.94	8.20
HBr	-	28.5	8.50	9.04	-
SO_2	34.2	39.0	9.00	9.36	8.40

According to our measurements, the compound of krypton with phenol has a melting point of 47°. We were unable to determine the fusion diagram for the system xenon-phenol, owing to the very small amount of xenon that was available to us. The determination of fusion diagrams for the systems A- and Kr-phenol is very difficult, owing to the high pressures.

The results in Table 4 show that the heats of formation of these compounds

are all very close to one another. The heats of formation of the compounds of phenol with H_2S and HBr, for which the molecular radii and Van-der-Waals forces are very similar, are almost identical.

For the compounds of H_2S, SO_2, and HCl with phenol we have established the formula 1 M: $3C_6H_5OH$. As the compounds of A, Xe, and Rn with phenol are isomorphous with the compounds of H_2S, SO_2, and HCl with phenol, they also must have the formula 1 M: $3C_6H_5OH$, which is confirmed also by the closeness of the values of heat of formation for the Xe, HCl, H_2S, and HBr compounds.

The close analogy in properties between the six compounds given in the table proves that their formation is brought about by the same type of chemical bond. For compounds of the inert gases, this bond can in the present case be only Van-der-Waals. Also, analogy between substances that are so different in the chemical sense can occur only when they enter in combination as whole molecules, which must have a definite resemblance to atoms of inert gases. The group of molecular compounds formed by phenon is evidently larger than that of molecular crystal-hydrates, for it includes also hydrogen halide compounds, which give hydroxonium compounds with water, and not crystal-hydrates. Compounds of this group are more stable than crystal-hydrates, for, at a coordination number of 3, they have almost the same heat of formation as the crystal-hydrates of coordination number 6.

SUMMARY

1. The compound of Rn with phenol is isomorphous with that of SO_2 with phenol. At 15°, the distribution constant of radon between the gas phase and the crystals of the SO_2 compound is 0.24. For the compound of H_2S with phenol, it is 1.24. Consequently, radon forms a phenol compound that is more stable than that of H_2S, and less stable than that of SO_2. The value of the dissociation pressure of the radon compound must lie between the values for the dissociation pressures of these latter compounds.

2. It is shown that the compounds of H_2S, SO_2, and HCl with phenol have the formula 1 M: $3C_6H_5OH$. The isomorphism of these compounds with compounds formed between the inert gases and phenol and the closeness of their heats of formation show that their formulas are analogous and that the same type of chemical bond is present.

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EXPERIMENTAL STUDY OF THE ELECTRON DENSITY IN CRYSTALS

COMMUNICATION 5. ELECTRON DENSITY OF Mg_2Si

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The determination of the electron density in the lattice of the chemical compound Mg_2Si was carried out with the object of studying the character of the chemical linkage of the atoms in this compound. Mg_2Si is a member of the group of compounds formed by magnesium with elements of the fourth group: silicon, germanium, tin, and lead (Mg_2Si, Mg_2Ge, Mg_2Sn, and Mg_2Pb). The composition of these compounds is in accord with the usual rules of valency (the elements of the fourth group being here charged negatively); they all have the same crystal structure, anti-isomorphous to fluorspar, and they do not form solid solutions with their components, which is characteristic for ionic compounds. The physical properties of the compounds vary in regular manner as the atomic number of the anionic element is increased. For example, the melting point varies from 1102° for Mg_2Si to 780° for Mg_2Sn and 553° for Mg_2Pb, i.e., the stability of the compounds falls in this series. Affinity for electrons falls in the same sense, and the metallic properties of the anion elements become more marked. The electrical resistivity falls from $1096 \cdot 10^{-6}$ ohm/cm^3 for Mg_2Sn to $180 \cdot 10^{-6}$ ohm/cm^3 for Mg_2Pb (there are no data in the literature for Mg_2Si). An examination of these properties leads to the conclusion that the ionic character of the atomic linkage must be most pronounced in the compound Mg_2Si, and metallic character -- in the compound Mg_2Pb [1].

A study of the distribution of electron density permits the character of the chemical linkage of the atoms in the lattices of chemical compounds of this group to be more fully elucidated. The compound chosen for examination is a very convenient one from the point of view of the technique of electron density determination. Both components of the compound Mg_2Si are comparatively light elements of low atomic number, and from the friable compound it is easy to prepare fine powders that are stable in air. The phase diagram for the system Mg_2Si has been studied, and it has been shown that Mg_2Si is the only compound formed in this system and that it forms two eutectics with its components [2]. This compound does not form solid solutions.

EXPERIMENTAL

Preparation of the sample

An alloy corresponding to the chemical compound Mg_2Si was obtained by melting together magnesium and silicon in silica crucibles in a high-frequency furnace. First of all the silicon was melted (for this purpose the silica crucible was placed inside a graphite one), then the magnesium was added. A series of alloys of varying magnesium content were prepared. After preparing the alloys, they were annealed at 1000° for three days, and their microstructure was exam-

ined. On the basis of the results, the alloy was selected that was nearest in composition to the compound Mg₂Si, and it was analyzed for its magnesium content. The composition of the chosen alloy corresponded to a magnesium content of 63.34% by wt., the theoretical magnesium content for the compound Mg₂Si being 63.4% by wt. The experimentally determined lattice constant of the chemical compound is 6.338 ± 0.001 Å. This value of the constant differs from that obtained by Owen and Preston [3] and is in good agreement with the value obtained by Klemm and Westling [4]. Measurements of the lattice constants for alloys with an excess of one component above the stoichiometric proportion did not show any variation in the lattice constant of the chemical compound Mg₂Si, which points to the non-formation of solid solutions in the chemical compound.

The alloy corresponding to the chemical compound is very friable and has a blue color with a metallic luster. The powder for the preparation of the sample was ground up in a mortar, grinding being continued until continuous lines were formed on the X-ray photographs with sharp resolution of the α-reflection doublets of the higher orders.

Preparation of the X-ray photographs and their photometry.

The procedure for the preparation of the X-ray photographs was the same as that used by us previously [5]. They were obtained with copper radiation and a nickel filter, using plane and cylindrical samples. The latter served mainly for the determination of the intensity of the weak lines. The absorption of the cylindrical samples could not be taken into account because of the low values of the absorption coefficients of the scattering atoms, the small diameters (about 0.2-0.3 mm) of the samples, and the close reflection angles for the lines on the X-ray-gram that were to be compared. For the flat samples, the absorption was calculated by the formula:

$$A = \frac{\sin(2\theta - \alpha)}{\sin \alpha + \sin(2\theta - \alpha)},$$

where α is the angle between the incident ray and the plane of the sample (varying from 15 to 50°).

As the compound Mg₂Si gives rise to reflections that vary considerably in intensity [thus for planes for which $\underline{h} + \underline{k} + \underline{1} = 4\underline{n}$, $\Sigma = 4(Si + 2Mg)$; when $h + k + 1 = 4n \pm 1$, $\Sigma = 4Si$; and when $h + k + 1 = 4n \pm 2$, $\Sigma = 4(Si - 2Mg)$], it was essential to prepare a series of X-ray photographs of varying exposure. In cases where β lines fell on α lines and there was the possibility of the first passing through the nickel filter, attention was turned to the absence of β lines from the planes having the most intense reflection.

The photometry of the X-ray diagram was carried out at a magnification of 1:6. When the X-ray diagrams were prepared from flat samples, the determination of the intensity was made from the area of the peak on the photometric curve, which was determined, as previously, by weighing the peak, after redrawing on a logarithmic scale. The limit of the linear dependency of blackening on the X-ray intensity was verified for the film used. Blackening values exceeding the linear limit were not used for calculation purposes. The blackening of the ground of the X-ray photograph was taken into account also.

Determination of the absolute values of the atomic factor

Conversion from relative to absolute values of the atomic scattering factor was carried out with the aid of aluminum as a standard. The X-ray diagrams were prepared by the substitution method, using equal exposures for aluminum and

for the compound Mg_2Si. The comparison was carried out for reflections from planes (331) and (422) of aluminum and (620) and (642) of the compound Mg_2Si. The values for the atomic factors of aluminum obtained by James, Brindle, and Wood [6] were taken as standard.

The calculation was performed by the formula:

$$F_{1abs.} = \frac{f_1 \text{ rel.}}{f_2 \text{ rel.}} \cdot \frac{N_2}{N_1} \sqrt{\frac{\mu_1 t_2}{\mu_2 t_1}} F_{2abs.} \,,$$

where the subscript (1) relates to data for Mg_2Si and the subscript (2) to data for aluminum. All the symbols have their usual significance, and

$$N = 1/\underline{v} = 1/a^2,$$

For Mg_2Si, $\underline{a} = 6.338$ A; and for aluminum, $\underline{a} = 4.041$ A. The exposure ratio $t_2:t_1$ = 1:1. For aluminum in copper radiation, $\mu = 131.5$; for the compound Mg_2Si in copper radiation, μ was calculated according to the formula:

$$\left(\frac{\mu}{\rho}\right)_{Mg_2Si} = 0.366\left(\frac{\mu}{\rho}\right)_{Si} + 0.634\left(\frac{\mu}{\rho}\right)_{Mg} = 47.81$$

whence $\mu_{Mg_2Si} = 47.81 \times 2 = 95.62$, since the density of Mg_2Si determined from the X-ray-structure results has the value 2.00; the pycnometrical value is 2.01. The values of $\frac{\mu}{\rho}$ for magnesium, aluminum, and silicon are taken from the reference literature [7].

Inserting the calculated values into the equation already cited, we obtain:

$$F_{abs._{Mg_2Si}} = F_{abs._{Al}} \cdot 3.29 \frac{f_{rel._{Mg_2Si}}}{f_{rel._{Al}}}$$

The comparisons were made in pairs — for planes (331) aluminum and (620) Mg_2Si, and (422) aluminum and (642) Mg_2Si. The determination of the factor for converting relative into absolute atomic factors was carried out on the basis of the results of three determinations. The results of these determinations are given in Table.1.

TABLE 1

Conversion of relative values of the structural factor into absolute values

No. of determination	Results for aluminum				Results for Mg_2Si			
	hkl	I/A	$f_{rel.}$	F_{abs}	hkl	I/A	$f_{rel.}$	$F_{abs.}$
1	422	391	2.70	4.16	620	319	3.12	13.18
	331	374	3.24	3.29	642	590	2.44	10.16
2	422	282	2.29	4.16	620	193	2.43	12.52
	331	251	2.65	3.29	642	382	1.97	9.63
3	331	415	3.41	4.16	620	346	3.25	13.04

Mean value: $F_{abs.620} = 12.91$; $F_{abs.642} = 9.90$.

The results in this table served further for the conversion of the relative atomic factors into absolute. The dispersion correction was made from Hönl's results [8].

TABLE 2

Determination of the absolute values of F for the compound Mg_2Si

hkl	$\sin\theta$	$\sin\theta/\lambda$	$F_{\lambda Cu}$ rel.	$F_{\lambda Cu}$ abs.	e^{-M}	$\Delta f \cdot e^{-M}$	F_{020} abs.
111	0.210	0.136	59.5	10.33	0.957	0.17	10.16
200	0.243	0.158	42.5	7.38	0.943	0.11	7.27
220	0.343	0.223	130.0	22.58	0.889	0.43	22.15
311	0.403	0.262	45.5	7.90	0.850	0.15	7.75
222	0.420	0.273	31.7	6.43	0.838	0.10	6.33
400	0.485	0.315	115.4	20.04	0.790	0.38	19.66
331	0.529	0.344	40.7	7.07	0.756	0.14	6.93
420	0.543	0.353	28.5	4.95	0.745	0.09	4.86
422	0.595	0.386	100.1	17.37	0.702	0.34	17.03
511(333)	0.631	0.410	36.0	6.25	0.672	0.12	6.13
440	0.687	0.446	85.6	14.87	0.624	0.30	14.57
531	0.718	0.466	31.2	5.42	0.597	0.11	5.31
600(442)	0.728	0.473	–	3.50[1]	0.588	0.07	3.43
620	0.768	0.499	74.2	12.89	0.577	0.28	12.61
533	0.796	0.517	–	5.00[1]	0.531	0.10	4.90
622	0.805	0.523	–	2.80[1]	0.523	0.06	2.74
444	0.841	0.546	66.3	11.52	0.493	0.24	11.28
711(551)	0.867	0.563	24.6	4.27	0.472	0.08	4.19
640	0.875	0.569	–	2.40[1]	0.465	0.06	2.34
642	0.908	0.590	57.0	9.90	0.438	0.21	9.69

[1] Values obtained by graphical interpolation.

Results for the determination of F-values for the compound Mg_2Si are given in Table 2. In the graph (Fig. 1) F_{020} is given in absolute units for a temperature of 20°, and curves are given, according to the various planes, of $F = 2f_{Mg} + f_{Si}$, $F = f_{Si}$, $F = f_{Si} - 2f_{Mg}$.

Calculation of the characteristic temperature

There are no data in the literature concerning the characteristic temperature of Mg_2Si, and this quantity was determined by calculation from Lindeman's equation, which involves the melting point [9]. The characteristic temperature:

$$\theta = c\sqrt{T_S/av^{2/3}},$$

where a is the atomic weight, v the atomic volume, T_S the absolute temperature at the m.p., and c is a constant, taken to be 137. For the calculation of the characteristic temperature of Mg_2Si, the following values were assumed: M.p. 1373°K, atomic volume of magnesium 14.1 and of silicon 12.0, mean atomic weight 25.57. From these data the characteristic temperature of Mg_2Si was calculated to be 423°.

Calculation of the temperature factor

When introducing the dispersion correction, the temperature factor is calculated from the formula:

$$F_1 = F_0 \cdot e^{-\beta_{ch^2}} = F_0 \cdot e^{-M},$$

where

$$M = \frac{6h^2}{mk\theta}\left[\frac{\Phi(x)}{x} + \frac{1}{4}\right]\frac{\sin^2\theta}{\lambda^2}.$$

Here the following values are assumed for the constants:

$$h = 6.55 \cdot 10^{-27}; \quad m_n = 1.662 \cdot 10^{-24}; \quad k = 1.371 \cdot 10^{-16}.$$

When recalculating the absolute values of the atomic factors, obtained for 20°, for higher temperatures in order to establish convergency of the Fourier series, the following formula was used:

$$F_1 = F_{20} \cdot e^{-\beta_{ch^2}},$$

where

$$\beta = \frac{6h^2}{mk\theta}\left\{\frac{\Phi\left(\frac{\theta}{T}\right)}{\frac{\theta}{T}} - \frac{\Phi\left(\frac{\theta}{T_{20}}\right)}{\frac{\theta}{T_{20}}}\right\}.$$

Figure 1. The F-curve for the compound Mg₂Si.

The assumed values of the constants were the same as before.

Calculation of electron density

The calculation of electron density was carried out for a temperature of 4800°K. Atomic factor values for this temperature are given in Table 3.

TABLE 3

Atomic factors recalculated for a temperature of 4800°K

hkl	F_{020}abs.	e^{-M}	F_{4800}
111	10.16	0.802	8.14
200	7.27	0.745	5.42
220	22.15	0.555	12.30
311	7.75	0.445	3.45
222	6.33	0.414	2.62
400	19.66	0.308	6.06
331	6.93	0.247	1.71
420	4.86	0.230	1.12
422	17.03	0.171	2.91
511(333)	6.13	0.137	0.84
440	14.57	0.095	1.38
531	5.31	0.077	0.41
600(442)	3.43	0.071	0.24
620	12.61	0.053	0.06
533	4.90	0.042	0.21
622	2.74	0.039	0.11
444	11.28	0.029	0.33
711(551)	4.19	0.023	0.10
640	2.34	0.022	0.05
642	9.69	0.016	0.16

Figure 2. Unit cell of the compound Mg₂Si.

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The minimum value of the atomic factor used in the calculation is about 2% of its value at 20°, and is not outside the limits of the accuracy of measurement. At the calculation temperature indicated, the distribution of electron density in the interionic space is free from any effect due to the breaking off of the series.

TABLE 4

Electron density in the [100], [110], [111] and [001]$_{3/4\ 3/4}$ directions of the unit cell of the compound Mg_2Si.

Distance in Å	Electron density in el./Å³	Distance in Å	Electron density in el./Å³
a) [100]—AB		c) [110]—AC	
0.00	10.53	0.00	10.53
0.63	2.75	0.45	4.67
1.27	0.36	0.90	1.06
1.58	0.22	1.34	0.32
1.90	0.09	1.79	0.19
2.54	0.06	2.24	0.19
3.17	0.00		
b) [111]—AD		d) [001]$_{3/4\ 3/4}$—EF	
0.00	10.53	0.00	0.20
0.55	3.56	0.32	0.60
1.10	0.54	0.63	0.75
1.37	0.33	0.95	2.49
1.48	0.28	1.27	6.59
1.54	0.22	1.58	2.49
1.59	0.21	1.90	0.75
1.65	0.50	2.54	0.60
2.20	3.15	3.17	0.20
2.7	6.59		
3.30	3.13		
3.85	0.41		
4.40	0.10		
4.95	0.00		
5.50	0.00		

The calculation was carried out with the aid of the triple Fourier series:

$$\rho = \sum_{-\infty}^{+\infty}\sum\sum A_{hkl} \cdot \cos 2\pi \left(h\frac{x}{a} + k\frac{y}{a} + l\frac{z}{a} \right).$$

There are 536 terms in the series. For convenience of calculation we shall take a as having the value 10, and since

$$A_{hkl} = \frac{1}{V} \cdot F_{hkl} = \frac{F_{hkl}}{a^3},$$

therefore

$$\rho = A_0 + \frac{4}{a^3}\left\{ F_{hkl} \cdot \cos 2\pi \left(h\frac{x}{10} + k\frac{y}{10} + l\frac{z}{10} \right) \right\}$$

and for $A_0 = \frac{4Si + 8Mg}{a^3}$ we have

$$\rho = 0.5965 +$$
$$+ 0.0157 \left\{ F_{hkl} \cdot \cos 2\pi \left(h\frac{x}{10} + k\frac{y}{10} + l\frac{z}{10} \right) \right\}.$$

In making the calculation it must be remembered that, for reflections for which $h+k+l = 4n \pm 2$, F is negative.

Results of the electron density calculation are given in Table 4. The directions for the calculation are shown in Fig. 2. The electron density results are shown graphically in Fig. 3 for the various directions in the unit cell, and in Fig. 4 for the (110) plane.

DISCUSSION OF RESULTS

The electron density calculations showed that the electron density in the lattice of the compound Mg_2Si has an irregular distribution. The interionic electron density in the (100) direction between the silicon ions (Fig. 3a) falls
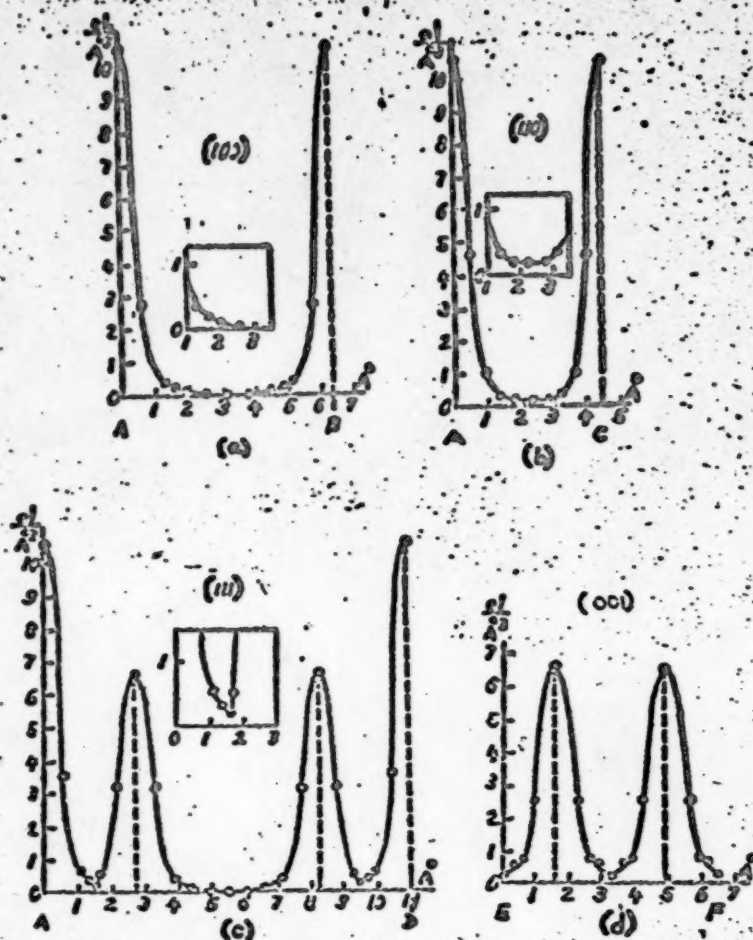
Figure 3. Electron density distribution in the directions: (a) (100)-AB; (b) (110)-AC; (c) (111)-AD; (d) (001)$\frac{3}{4}\frac{3}{4}$-EF.

to zero, indicating absence of conductivity electrons within the limits of the electron density calculations. In the (110) direction there is a higher electron density, 0.2 el./$\AA^3$ (Fig. 3b), which is to be attributed to homopolar bonds between these atoms. Similar electron density values are observed between the magnesium ions and between the ions of magnesium and silicon (Fig. 3c, 3d, and 4).

The electron density distribution around the magnesium ion has an asymetrical appearance contrasting with that around the silicon ion (Fig. 4).

On the basis of an examination of the crystal structure, physical properties, and positions of the elements in the periodic system for the series of compounds,

Mg_2Si, Mg_2Ge, Mg_2Sn, Mg_2Pb, the intermediate character of the chemical bond in this group of compounds — intermediate between ionic and metallic — was pointed out. The compound Mg_2Si is the extreme member of this group of chemical compounds and should, according to its position and properties, show ionic character in the bonds between its atoms to a considerable extent [1]. The electron density determination has shown that, as expected, conductivity electrons are absent in the lattice of the compound, while, at the same time, there are homopolar bonds present between the atoms, which are revealed by the higher electron density between the atoms, amounting to 0.2 el./Å^3. It was not considered possible to determine the degree of ionization of the magnesium and silicon atoms, owing to the absence of a sharp boundary between the separate ions.

Figure 4. Distribution of electron density in the plane (110).

SUMMARY

1. The experimental determination of the structural factors for an alloy, close in composition to the chemical compound Mg_2Si, has been carried out.

2. The electron density distribution for four directions of the unit cell of the compound Mg_2Si has been calculated by the triple Fourier series method at a calculation temperature of 4800°K.

3. The results obtained indicate an irregular distribution of electron density in the interionic space. Between the silicon ions in the (110) direction, between the magnesium ions, and between the ions of magnesium and silicon, a higher electron density is to be observed, amounting to 0.2 el/Å^3. Between the silicon ions in the (100) direction, the electron density falls to zero.

4. In contrast to the silicon ion, the magnesium ion has an asymmetrical appearance with respect to electron density distribution.

5. The higher electron density between the atoms points to the presence of homopolar links in the lattice of the compound. The zero electron density in certain parts of the lattice points to the almost complete absence of conductivity electrons.

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KINETICS OF THE POLYMERIZATION OF COMPOUNDS
CONTAINING A CONJUGATED LINK

POLYMERIZATION OF METHYL ACRYLATE

P. S. Shantarovich

In the previous paper [1] the kinetics of the polymerization of chloroprene
were described. It was then pointed out that the concept that we have developed
concerning the polymerization of chloroprene may be extended also to other com-
pounds, in fact to those which contain a conjugated link. In this paper we de-
scribe results on the kinetics of the polymerization of methyl acrylate in the
mass (undiluted liquid), working at high degrees of conversion. The kinetics for
a low degree of conversion into polymer (3-4%) have been studied by Bagdasaryan [2].

EXPERIMENTAL

Experimental Results

The experimental arrangement and the initiation conditions were similar to
those used in the investigations on the polymerization of chloroprene. The re-
action was initiated by light from a mercury lamp. Chemically active radiation
(λ = 303-313 mμ) was filtered off by means of a 1.5-cm layer of 0.0005 $\underline{M}$-
K_2CrO_4. The reaction rate was measured by a dilatometric method. On illumin-
ating the reaction vessel, polymerization did not begin immediately, but after a
certain delay (about 1.5 min), it then proceeded at constant rate. An appre-
ciable increase in rate was to be observed at 8-10% conversion, and at X $\simeq$ 35%
the reaction went over into the stage of rapidly increasing rate. When the light
is switched off, intense dark polymerization is to be observed, and it proceeds
at a dwindling rate and, after a certain time, this attains a minimum value. The
rate then increases very slowly as polymer is formed right until a nucleus of
the insoluble form of the polymer arises in the polymerizing mass. The formation
of nuclei of the opaque granular mass of polymer proceeds at various points in
the reacting space. The formation of the nuclei, as regards number and the
places at which they form, proceeds in an irregular fashion, but the moment at
which nuclei arise is determined by the degree of conversion: when the reaction
has proceeded to the extent of about 30-33%, nuclei appear. From this moment,
the rate of polymerization sharply increases. The general kinetic picture of
the dark polymerization of methyl acrylate is presented in Figure 1, beginning
from the moment of switching off the light. The curves 1, 2, 3 and 4 were ob-
tained after 10, 19, 24, and 32 min. irradiation of the polymerizing mass; at
the end of this period the light was switched off. The amounts of polymer
formed up to the moment when the light was switched off are respectively 7.5,
14, 18, and 24.5%. The further the photoreaction has gone, the shorter the

period of the slow dark reaction. Thus, the kinetics of the formation of poly-methyl methacrylate are precisely similar to those described by us previously [1] for the polymerization of chloroprene, though with this difference, that the point for the transition of the slow dark reaction into the non-stationary condition lies at about 31-32% conversion, instead of at 9-10% for chloroprene. Also, in contrast with the chloroprene polymerization, the character of the curves for the dark polymerization of methyl acrylate does not depend on the extent of the photo-reaction (i.e. on X_{phot}). All the curves can be fully superimposed. In all cases the same end-product is formed.

Fig. 1. Kinetics of the dark polymerization of methyl acrylate at 20°: 0) photo-reaction; 1) t_e 10 min., X_{phot} 7.5%; 2) t_e 19 min., X_{phot} 14%; 3) t_e 24 min., X_{phot} 18%; 4) t_e 32 min., X_{phot} 24.5%.
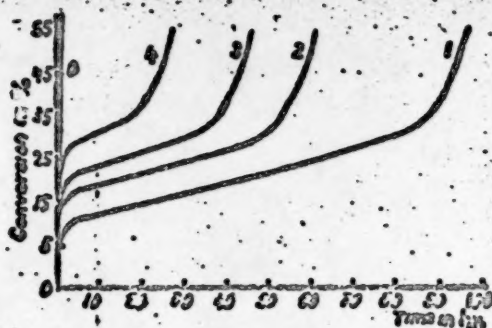
This particular circumstance permitted the observance of an essential fact, the observance of which was impossible in the polymerization of chloroprene[1]) namely that the minimum rate (v_{min}) of the dark polymerization depends on the value of X_{phot} — the amount of polymer formed at the moment when the light is switched off, or, what amounts to the same, on the value of X_{min} — the amount of polymer formed at the moment when the dark reaction reaches the minimum rate.

From these results it is evident that the minimum rate may be expressed by the formula:

$$v_{min} = ZX_{min}^n. \tag{1}$$
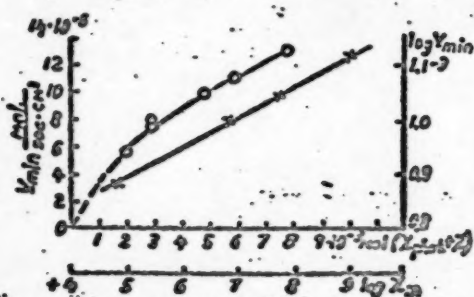
Fig. 2. Dependence of the minimum rate of the dark polymerization on the amount of polymer at the moment of minimum rate.

X_m in mol.	$v_{min} \cdot 10^{-6}$ mol./sec·cm³	
	Calculated	Found
0.00295	0.0077	0.0077
0.00473	0.0102	0.0098
0.0058	0.1010	0.0109
0.0079	0.0130	0.0127

[1]) Because of the superposition of the process of ω-formation on the preceding process of μ-polymerization.

This relation is shown on Fig. 2, and in this figure is shown also the relation between $\log \underline{v}_{min}$ and $\log X_{min}$, whence we find that $\underline{n} = 0.53$ and $Z = 1.42 \cdot 10^{-7}$. Hence, the exact expression for the minimum rate has the form:

$$\underline{v}_{min} = 1.42 \cdot 10^{-7} \sqrt{X_m} \qquad (2)$$

Formula (2) corresponds closely to the experimental observations.

Discussion of Results

Switching off the light, i.e. curtailing the formation of active centers from outside, does not result in the complete stoppage of the polymerization of methyl acrylate. The reaction, having reached a certain minimum rate, continues to develop. In conformity with the chain-branching nature of the process, the change in the number of active centers (growing chains) with time may be represented by the equation:

$$\frac{dn}{dt} = \underline{f}n - k_5 n^2.$$

After transformation and integration we find that the rate as a function of the X-quantity of forming polymer tends to a constant value:

$$\underline{v}_{min} = \frac{k_4 \underline{f}}{k_5} \qquad (3)$$

The experimental value of the minimum rate is given by Formula (2), and therefore

$$\frac{k_4 \underline{f}}{k_5} = 1.4 \cdot 10^{-7} \sqrt{X_m}, \qquad (4)$$

i.e. the minimum rate, which is determined by the concentration of centers $\underline{n} = \frac{\underline{f}}{k_5}$, rises, with the extent of polymerization proportional to the root of the quantity of polymer that has been formed.

The relation (4) is possible only under the condition that: $k_5 = \dfrac{k_0}{\sqrt{X_m}}$, (5)

for neither the rate of chain growth nor the branching of the chains is determined by the amount of polymer that has been formed.

Hence, the kinetics of the slow dark reaction, which we regard as the reaction of the formation of the three-dimensional structure of the polymer, must be described by the differential equation:

$$\frac{dn}{dt} = \underline{f}n - k_0 X^{-\frac{1}{2}} n^2. \qquad (6)$$

Integrating Equation (6) and assuming that $\dfrac{k_4 \underline{f}}{k_0} = 1.42 \cdot 10^{-7}$, the rate of formation of the insoluble form of the polymer of methyl acrylate can be calculated, using the kinetic curves for the polymerization (Fig. 1). The result of the exact calculation is shown in Fig. 3 (broken lines). The photo-reaction ($\underline{v}_{phot}$) is represented by a curve that proceeds from the origin; $\underline{v}_{phot}$ in the stationary phase of the reaction has a value of $1.38 \cdot 10^{-6}$ mol./sec·cm³. Switching off the light (arrow) causes a fall in rate, which evidently results from a recombination of chains in the mass of the liquid phase. The process proceeds in space by a branching out of the polymer structure. As this structure develops, the rate of the curtailment of growing chains varies according to the law $k_5 X^{\frac{1}{2}} = const.$ The broken curves in Fig. 3 demonstrate the accuracy with which this relationship holds.

Fig. 3. Rate of the dark polymerization
of methyl acrylate: 1) X_{phot}7.5%; 2)
X_{phot}14%; 3) X_{phot}18%; 4) X_{phot}24.5%

SUMMARY

1. It is shown that the mechanisms of the polymerization of methyl acrylate and of chloroprene are of the same type, i.e. that of compounds that contain a system of conjugated bonds. The resemblance between the two processes is emphasized by the heats of the reaction, which are equal (18.7 kcal) [3]. The magnitude of the heat effect is to be related to the loss of the energy of conjugation in the original monomer when the system is transformed from the initial ($R_n + M$) into the final ($R_n + 1$) state.

2. A differential equation describing the kinetics of the formation of the branched three-dimensional polymer structure has been obtained.

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INVESTIGATION OF SOLUBILITY IN THE RECIPROCAL SYSTEM

$CaSO_4 - KCl - H_2O$ AT 55°.

V.N. Sveshnikova

By a study of solubility in the quaternary reciprocal system [$CaSO_4$ + $2KCl \rightleftharpoons K_2SO_4$ + $CaCl_2$]--H_2O at 55 and at 25° by the isothermal method it has been possible to establish the composition of the solid phases formed as a result of double-decomposition reactions and to give an explanation of the origin of the calcium chloride found in certain brines. The reaction that lies at the basis of the reciprocal system is accompanied by the formation of the double salt syngenite, $CaSO_4 \cdot K_2SO_4 \cdot H_2O$ [1]:

$$2CaSO_4 \cdot 2H_2O + 2KCl = CaSO_4 \cdot K_2SO_4 \cdot H_2O + CaCl_2 + 3H_2O.$$
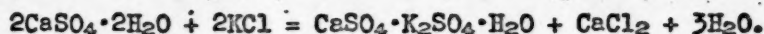
It should be noted that a similar interaction between sodium chloride and calcium sulfate is not observed [2].

The reciprocal system $CaSO_4 - KCl - H_2O$ includes the following four ternary systems: 1) $KCl - CaCl_2 - H_2O$; 2) $CaSO_4 - CaCl_2 \quad H_2O$; 3) $K_2SO_4 - CaSO_4 - H_2O$; 4) $K_2SO_4 - KCl - H_2O$.

Ternary System $K_2SO_4 - CaSO_4 - H_2O$ at 55°

The ternary system potassium sulfate--calcium sulfate--water has been studied by many authors over a wide interval of temperature. Isotherms for 40, 60, and 100° were obtained by Hill [3]. This author carries out a detailed study of this system and gives its polytherm. In his investigations, Hill [3] takes up a critical attitude towards the work of van't Hoff on the determination of the transition points in the system calcium sulfate--water, and he gives 42° as the temperature for the transition gypsum-anhydrite, i.e., 21° lower than that found by van't Hoff (63°) [8]. Potassium sulfate lowers the solubility of calcium sulfate, and two double salts are formed: syngenite, $K_2SO_4 \cdot CaSO_4 \cdot H_2O$ and potassium pentacalcium sulfate, $5CaSO_4 \cdot K_2SO_4 \cdot H_2O$. In view of the long time required for establishment of equilibrium in systems containing calcium sulfate, the study of solubility was carried out using already prepared solid phases, i.e., an artificially prepared salt or mixture of salts was mixed in a vessel, and a liquid phase of known concentration was poured in. The solutions were allowed to stand in a thermostat for 8-10 days. The solid phases were identified by optical examination of the crystals. K, Ca, and SO_4 were determined in the liquid phase by the usual gravimetric methods. The results of the experiments are given in Table I. The solubility diagram consists of four branches (Fig. 1). The branch AB, which corresponds to the solubility of anhydrite $CaSO_4$, is lowered somewhat under the influence of potassium sulfate K_2SO_4. The branch BC, within the limits of 4-6% K_2SO_4, corresponds to the solubility of potassium pentacalcium sulfate,

$5CaSO_4 \cdot K_2SO_4 \cdot H_2O$; the branch CD to syngenite, $K_2SO_4 \cdot CaSO_4 \cdot H_2O$. The composition at all the points given on the diagram was obtained experimentally, with the exception of the point for the simultaneous crystallization of anhydrite and pentasulfate, which was obtained graphically and verified synthetically. The lines joining the points for the compositions of the double salts (syngenite and pentasulfate) to the origin do not pass through the corresponding crystallization branches; hence, both salts dissolve incongruently.

TABLE 1

Solubility isotherm at 55° for the system $K_2SO_4 - CaSO_4 - H_2O$

No.	Liquid phase (wt.%)					Solid phase (by optical examination of crystals)	Duration of expt. in days
	K˙	SO_4"	Ca˙˙	K_2SO_4	$CaSO_4$		
1	–	–	0.054	–	0.183	Anhydrite	8
2	0.56	0.81	0.036	1.30	0.129	Anhydrite	22
3		5.42	0.012	9.83	0.033	Syngenite	15
4	2.26	2.84	0.032	5.02	0.108	Pentasulfate	16
5	6.76	8.32	0.005	15.09	0.007	Syngenite + K_2SO_4	13
6	2.69	3.25	0.028	5.92	0.095	Pentasulfate + syngenite	26
7	1.19	1.62	0.035	2.94	0.125	Anhydrite	20
8	1.93	–	0.032	4.20	0.120	Anhydrite + pentasulfate	20
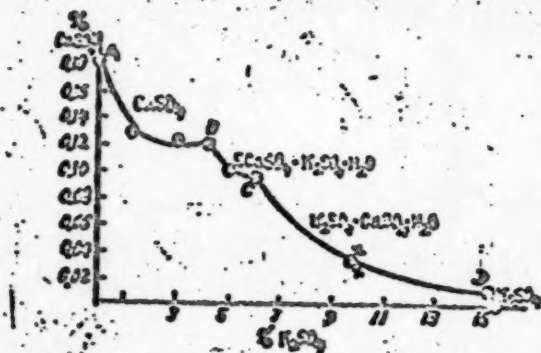
Fig. 1. Solubility isotherm at 55° for the system $K_2SO_4 - CaSO_4 - H_2O$

The formation of pentasulfate (Fig. 2) at this temperature from anhydrite, as also its decomposition into anhydrite, evidently proceeds through a stage in which syngenite is formed (microscopical observations).

The crystal-optical constants of syngenite are

Ng = 1.518; Nm = 1.517; Np = 1.501

The crystal-optical constants of potassium pentacalcium sulfate are

Ng = 1.568; Nm = 1.569; Np = 1.556 (Lyashenko).

Ternary system $CaSO_4 - CaCl_2 - H_2O$ at 55°

This system was studied at 55° both in the stable and in the metastable state (Fig. 3). The metastable diagram consists of the solubility branches of dihydrate gypsum, $CaSO_4 \cdot 2H_2O$, α-hemihydrate, $\alpha-CaSO_4 \cdot \frac{1}{2} H_2O$, and calcium chloride dihydrate, $CaCl \cdot 2H_2O$ [9]. It is interesting to note that, under the influence of calcium chloride, the solubility of gypsum first falls from 0.2 to 0.02% $CaSO_4$, and then rises to 0.1%. It is difficult to say how this is to be explained.

The stable diagram consists of the solubility branch of anhydrite, $CaSO_4$, and that of calcium chloride dihydrate, $CaCl_2 \cdot 2H_2O$. At 55° the solubilities of gypsum and anhydrite do not differ greatly, and this explains the closeness of

the branches for the stable and metastable phases. The high stability of the metastable forms of gypsum at this temperature should be noted (Table 2).

<div align="center">TABLE 2</div>

<div align="center">Solubility isotherm at 55° for the system $CaCl_2$ – $CaSO_4$ – H_2O</div>

No.	Liquid phase (wt. %)						Solid phase [1]
	Ca··	Cl'	SO_4''	$CaCl_2$	$CaSO_4$	H_2O	
1	2.82	5.26	0.102	8.23	0.102	91.67	Gypsum $CaSO_4 \cdot 2H_2O$
2	3.31	5.78	0.068	9.08	0.097	90.82	Gypsum $CaSO_4 \cdot 2H_2O$
3	4.85	8.66	0.053	13.55	0.075	86.38	Gypsum $CaSO_4 \cdot 2H_2O$
4	8.13	14.70	0.022	23.00	0.030	76.97	Gypsum $CaSO_4 \cdot 2H_2O$
5	9.78	17.52	0.015	27.08	0.020	73.97	Gypsum $CaSO_4 \cdot 2H_2O$
6	11.01	20.41	0.011	31.91	0.016	68.07	Gypsum $CaSO_4 \cdot 2H_2O$
7	15.35	27.35	0.043	42.50	0.061	57.44	Gypsum $CaSO_4 \cdot 2H_2O$
8	17.41	30.49	0.065	47.47	0.090	52.14	α-$CaSO_4 \cdot \frac{1}{2} H_2O$
9	18.23	32.14	0.029	50.45	0.040	49.51	α-$CaSO_4 \cdot \frac{1}{2} H_2O$
10	18.57	32.71	0.007	51.30	0.010	48.69	α-$CaSO_4 \cdot \frac{1}{2} H_2O$
11	20.45	36.38	0.022	56.94	0.030	43.03	$\begin{cases} CaCl_2 \cdot 2H_2O \\ \alpha\text{-}CaSO_4 \cdot \frac{1}{2} H_2O \end{cases}$
12	3.04	5.73	0.050	8.42	0.075	91.51	Anhydrite
13	9.55	17.62	0.009	27.0	0.013	73.00	Anhydrite

[1]) The solid phase was determined crystallo-optically by Lyashenko.

<div align="center">Ternary System KCl – $CaCl_2$ – H_2O at 55°</div>

The system has been investigated by a number of authors at various temperatures. The various authors have held diverse opinions about the chemistry of the system. Thus there was the suggestion of the possibility of the existence of the compound $KCl \cdot CaCl_2 \cdot 6H_2O$, analogous to carnallite, which was made in the Trans. State Inst. Appl. Chem by Shoykhet and Lukyanova [4], who studied the system over a wide range of temperatures (from −10 to 130°) in connection with its application to the treatment of the mother liquors of chlorate manufacture for separation of calcium chloride. Later, Lightfoot [5] found a double salt of composition $2KCl \cdot CaCl_2 \cdot 2H_2O$ at 35 and 75°.

In 1950, Assarsson [6] again investigated the system in detail and gave its polytherm; with the aid of Schreinemakers' method, he succeeded in proving that the double salt obtained has the composition $CaCl_2 \cdot KCl$.

Figure 3. Solubility isotherm at 55° for the system $CaCl_2$ – $CaSO_4$ – H_2O.

Dergunov and Bergman [7] found this double compound in melts of the salts. In our solubility investigation on the ternary system at 55°, we have established the existence of three crystallization branches: that of KCl, that of $CaCl_2 \cdot 2H_2O$, and that of the double salt, $KCl \cdot CaCl_2$ (Figure 4).
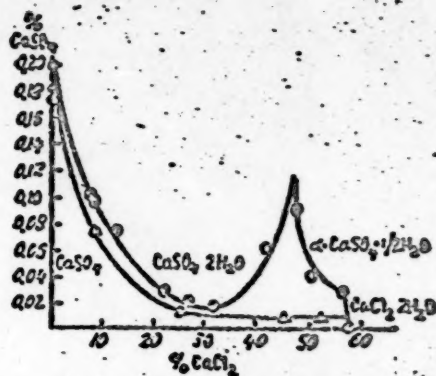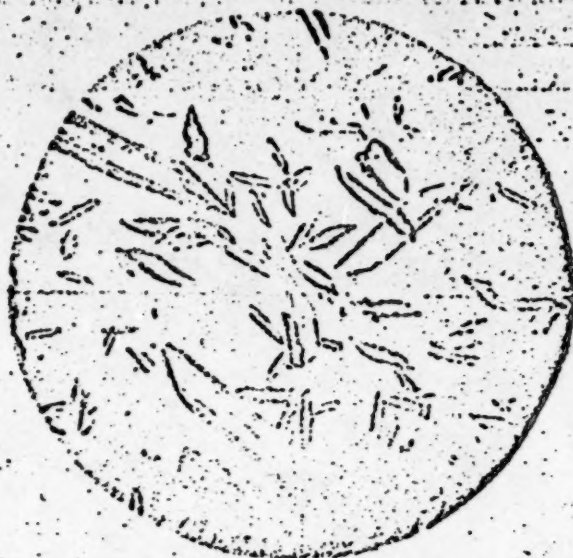
Fig. 2. Potassium pentacalcium sulfate
$5CaSO_4 \cdot K_2SO_4 \cdot H_2O$. (x 250).

Fig. 5. Hydrophylite. $KCl \cdot CaCl_2$. (x 250)

TABLE 3
Solubility isotherm at 55° for the system KCl - CaCl$_2$ - H$_2$O.

No.	Liquid phase (wt. %)					Solid phase
	Ca''	K'	Cl'	CaCl$_2$	KCl	
1	19.98	2.43	37.51	55.26	4.63	CaCl$_2$·2H$_2$O
2	20.37	2.34	37.90	56.40	4.46	CaCl$_2$·2H$_2$O + KCl·CaCl$_2$
3	1.74	13.44	15.20	4.82	25.66	KCl
4	11.40	3.33	3.05	31.55	6.35	KCl
5	14.51	2.72	28.07	40.18	5.11	KCl
6	4.60	9.63	16.48	12.75	18.27	KCl
7	11.52	3.18	23.48	31.89	6.07	KCl
8	—	—	—	49.35	7.79	KCl·CaCl$_2$; KCl

The double salt KCl·CaCl$_2$, which was investigated crystallo-optically for the first time by Lyashenko, corresponds to the little studied natural mineral hydrophylite (Ng = 1.572, Np = 1.526) (Fig. 5). The temperature limits for the existence of KCl·CaCl$_2$, according to the results of the last authors, are from 37.8° to fusion. The salt is difficult to separate because of the high viscosity of the solutions from which it is prepared. The results of the experiments are given in Table 3.
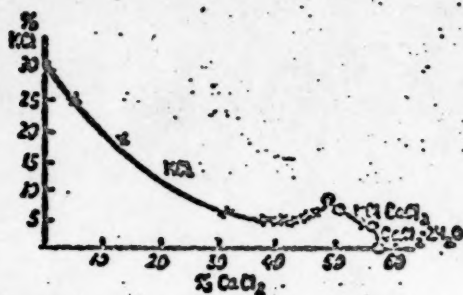
Fig. 4. Solubility isotherm at 55° for the system CaCl$_2$ - KCl - H$_2$O.
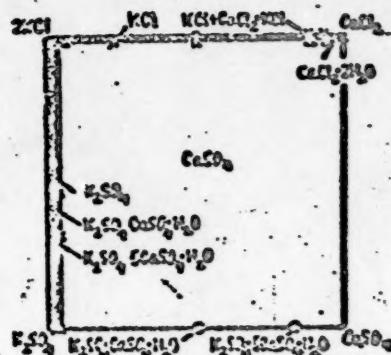
Fig. 6. Solubility isotherm at 55° for the system CaSO$_4$ - KCl - H$_2$O.

The Reciprocal System CaSO$_4$ - KCl - H$_2$O at 55°

The system was first studied by the author at 25° in 1947 [9]. At 55° the solubility diagram consists of the following fields (Figure 6):

1) the field of anhydrite CaSO$_4$, which occupies the greater part of the area — 96.50% of the whole area of the square;

2) the field of pentasulfate, which is immediately adjacent to the field of anhydrite: 0.66% of the whole area of the square;

3) the field of syngenite, which is between the fields of anhydrite and K$_2$SO$_4$;

4) the field of potassium sulfate, which is small in size and is adjacent, on the one side, to the field of syngenite, and on the other side — to the field of potassium chloride: 0.32%;

TABLE 4

Solubility isotherm at 55° for the reciprocal system CaSO₄ - KCl - H₂O

No.	Comp. of liquid phase in % by wt.					Comp. of liquid phase in ion-equiv.				
	K_2	Ca	Cl_2	SO_4	H_2O	K_2	Ca	SO_4	Cl_2	H_2O per 1000 ion-equiv.
1	2.34	20.37	37.90	——	39.39	5.56	94.44	——	100.00	4062.0
2	6.76	0.005	—	8.32	84.91	99.88	0.12	100.00	——	54.517
3	2.69	0.03	—	3.25	94.03	97.86	2.14	100.00	—	148.477
4	1.93	0.03	—	2.37	95.67	97.05	2.95	100.00	—	208.808
5	16.40	——	14.36	0.71	68.53	100.00	——	3.53	96.47	18.124
6	15.71	0.007	14.04	0.71	69.47	——	0.86	3.60	96.40	18.901
7	8.81	0.04	5.48	3.52	82.15	99.11	0.89	32.16	67.83	40.022
8	11.69	0.02	10.09	0.27	77.93	99.66	0.34	1.94	98.06	29.827
9	——	0.01	8.35	2.84	76.38	99.87	0.13	20.05	79.95	28.785
10	5.44	0.06	4.55	0.81	89.14	97.69	2.31	11.62	88.38	68.823
11	3.21	0.03	1.16	2.37	93.23	98.38	1.62	60.09	39.91	125.126
12	2.65	0.04	1.18	1.77	94.36	96.86	3.14	52.54	47.46	149.510
13	8.25	0.06	5.38	2.94	83.37	98.71	1.29	28.75	71.25	43.490
14	2.50	0.04	0.79	2.10	94.57	96.99	3.11	66.25	33.75	159.060
15	16.08	0.45	15.81	0.11	67.55	94.82	5.18	0.50	99.50	172.894
16	3.19	0.05	1.93	1.42	93.41	96.91	3.09	35.14	64.85	123.340
17	5.65	0.09	4.82	0.65	88.79	96.79	3.21	9.05	90.95	66.024
18	9.05	4.60	16.00	0.09	70.00	50.22	49.78	0.43	99.57	17.130
19	1.98	19.98	37.15	0.005	40.89	4.84	95.16	0.02	99.98	4.331
20	4.24	18.09	36.21	0.005	——	10.73	89.27	0.02	99.98	—

5) the field of potassium chloride, bounded on one side by anhydrite and to a small extent by potassium sulfate, syngenite, and pentasulfate: 0.50% (thus the field of potassium chloride borders on all the other fields of the system, forming four triple points):

6) the field of calcium chloride, which has the lowest area of all the fields: 0.03% of the whole area of the square;

7) the field of the double salt KCl·CaCl₂, which borders on the KCl field, on the CaSO₄ field, and on the CaCl₂·2H₂O field.

Stable points of simultaneous crystallization within the system:

1. KCl; K₂SO₄; syngenite — composition in ion-%: 96.40 Cl₂; 3.60 SO₄; 0.86 Ca; 99.14 K₂.
2. KCl; syngenite; pentasulfate: 99.0 Cl₂; 1.0 SO₄; 88.0 K₂; 2.0 Ca.
3. KCl; pentasulfate; CaSO₄; 0.70 SO₄; 99.30 Cl₂; 3.3 Ca; 96.7 K₂.
4. KCl·CaCl₂; CaCl₂·2H₂O; CaSO₄; 0.70 SO₄; 99.3 Cl₂; 5.7 K₂; 94.3 Ca.
5. KCl; CaCl₂·KCl; CaSO₄; 7 fields of crystallization, 5 points denoting simultaneous crystallization of three phases, and 7 points denoting simultaneous crystallization of two phases. The fields within the system were delimited by the method of adding a third salt to the non-variant solutions of the ternary systems. The solutions were kept in a thermostat for 10-25 days. The average time required for establishment of equilibrium was 2 weeks, so long as the solution was stirred with the already prepared solid phases. At 55° equilibrium was established noticeably more rapidly than at 25°.

The reaction between calcium sulfate and potassium chloride in solution is usually accompanied by the formation, together with calcium chloride, of syngenite, whose solubility is less than that of anhydrite. This, of course, leads

TABLE 2 (continued)

Composition of solid phase	Time allowed for establishment of equilibrium (days)
$CaCl_2 \cdot 2H_2O$ + KCl	10
Syngenite + K_2SO_4	14
Pentasulfate + syngenite	14
Anhydrite + pentasulfate	14
KCl + K_2SO_4	14
Syngenite, KCl, K_2SO_4	10
Syngenite, K_2SO_4	25
Syngenite, KCl	45
Syngenite, K_2SO_4	21
Syngenite + pentasulfate	14
Syngenite	10
Anhydrite + pentasulfate	18
Syngenite	12
Pentasulfate	15
Anhydrite + KCl	
Anhydrite + Pentasulfate	18
Syngenite + Pentasulfate	8
Anhydrite + KCl	14
Anhydrite + $KCl \cdot CaCl_2$ + $CaCl_2 \cdot 2H_2O$	21
KCl + $KCl \cdot CaCl_2$ + $CaSO_4$	

to a displacement of the reaction from left to right.

The next stage of the reaction leads, under known conditions, to formation of pentasulfate $5CaSO_4 \cdot K_2SO_4 \cdot H_2O$. Whereas the formation of syngenite occurs over a wide range of temperature, from 0 to 100°, the formation of pentasulfate occurs at higher than 32° [8].

$$CaSO_4 \cdot K_2SO_4 \cdot H_2O + 4CaSO_4 = 5CaSO_4 \cdot K_2SO_4 \cdot H_2O.$$
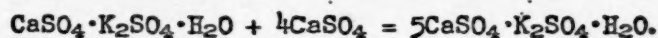
On comparing the solubility diagrams for 55° with those for 25° [9], we are led to the conclusion that:

1. Rise in temperature has a negative action on the double-decomposition reaction between $CaSO_4$ and KCl, for the syngenite field shrinks relative to the other crystallization fields, and the solubility of syngenite therefore increases [9]. However, the solubility of anhydrite falls with rise in temperature, which confirms the view expressed earlier, that this reaction has a negative temperature coefficient.

2. The number of separate fields in the system increases as the temperature rises. At 25° the double salts, pentasulfate and hydrophylite, are absent [9].

3. At 25° the stable form of calcium sulfate is dihydrate gypsum, whereas at 55° it is anhydrite.

In order to see whether a double-decomposition reaction is possible between $CaSO_4$ and KCl in the solid state under the influence of pressure, the molecular

volumes of the initial and final substances in the reaction $CaSO_4 + 2KCl \rightleftharpoons K_2SO_4 + CaCl_2$ were calculated. The molecular volume calculation showed that increase in pressure should not favor the formation of calcium chloride and syngenite. Actually, experiments carried out with a hydraulic press, using pressures of up to 20 T, confirmed the theoretical calculations:) no calcium chloride was formed in the mixtures subjected to pressure.

The facts obtained as a result of the study of the reciprocal system made an approach possible to the question of the formation of calcium chloride in natural brines. The occurrence of calcium chloride in natural lakes of the second class (Kurnakov's classification) is usually explained on the basis of the following double-decomposition reactions:

1) Kurnakov's reaction:

$$2Ca(HCO_3)_2 + MgCl_2 = CaCl_2 + CaMg(CO_3)_2 + 2H_2O;$$
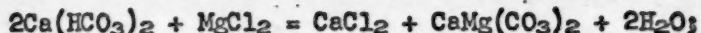
2) the cation-exchange reaction:

Ca --aluminum silicate + $MgCl_2 \rightleftharpoons Mg$ - aluminum silicate + $CaCl_2$.
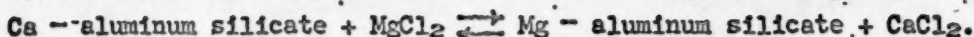
Urazov [11] investigated the Bakin lakes of the Apsheron peninsula and found them to contain a large amount of calcium chloride, reaching 12%. In the Perekop lakes of the Crimea, the $CaCl_2$ content is less and varies from 0.2 to 2.2%. Kurnakov [10] explains the excess calcium ion in the latter by the first double-decomposition reaction. In the Solikam salt deposits, potassium chloride is found in paragenesis with anhydrite. In his investigations of this deposit, Morachevsky [12] established the presence of calcium chloride to the extent of 0.3-3.3% in the zone of crystallization of potassium salts, but, as the author points out, no calcium chloride is found in the zone of crystallization of rock salt. Since the predominating calcium compound in this salt deposit is anhydrite ($CaSO_4$), the presence of calcium chloride in the zone of crystallization of potassium salts may be explained by the double-decomposition reaction:

$$2CaSO_4 + 2KCl + H_2O = CaSO_4 \cdot K_2SO_4 \cdot H_2O + CaCl_2,$$
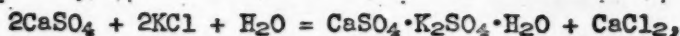
which occurred during the drying-up of the Perm sea, when the salt layers of the Higher Kama deposits were formed.

Interaction between potassium chloride and anhydrite can give considerable amounts of calcium chloride. Thus, at point C on Figure 6, where we have simultaneous crystallization of potassium chloride and anhydrite, the calcium chloride content of the liquid phase is as high as 12%. As this reaction proceeds further at lower temperatures, the possibilities of its occurrence in nature are widened. Although other double-decomposition reactions cannot be excluded for the Solikam deposits, the above considerations are confirmed by the following:

1) the occurrence of paragenesis of potassium chloride with anhydrite;

2) the presence of calcium chloride in the zone of crystallization of potassium salts and its absence in the zone of crystallization of rock salt.

SUMMARY

1. A study has been made of the solubility relations at 55° in the reciprocal system:

$$[CaSO_4 + 2KCl \rightleftharpoons K_2SO_4 + CaCl_2] - H_2O$$

52
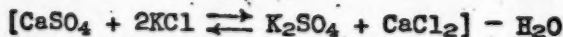
and in the ternary systems:

$KCl - CaCl_2 - H_2O$; $CaSO_4 - CaCl_2 - H_2O$; $CaSO_4 - K_2SO_4 - H_2O$.

2. In the reciprocal system 7 fields of crystallization have been established, and of these 3 correspond to double salts: syngenite, $K_2SO_4 \cdot CaSO_4 \cdot H_2O$; potassium pentacalcium sulfate, $5CaSO_4 \cdot K_2SO_4 \cdot H_2O$; and hydrophylite, $KCl \cdot CaCl_2$.

3. The formation of calcium chloride proceeds owing to the formation of the difficultly soluble double salt, syngenite.

4. Lowering of temperature favors the double-decomposition reactions.

5. The occurrence of calcium chloride in the zone of crystallization of potassium salts in the Solikam deposits may be explained, as can also other metamorphization reactions, by the double-decomposition reaction studied.

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CATALYTIC OXIDATION OF ETHYLENE ON MAGNESIUM CHROMITE

L. Ya. Margolis and O. M. Todes

In a previous work [1] we have studied the kinetics of the oxidation of iso-octane and ethylene in stream-form at catalysts belonging to the structural type of spinels (chromites, aluminates, etc.). The study under dynamic conditions of the determining stage of the oxidation process at various catalysts in presence of various additives does not seem possible. In this paper we give the results of a study of the oxidation of ethylene in a vacuum system under static conditions at low pressure (0.1-2 mm Hg). As under streaming conditions at catalysts of the type $Me^{II}M_2^{III}O_4$, the reaction goes to completion, i.e., to carbon dioxide and water.

EXPERIMENTAL

1. Gases

Ethylene was prepared by the dehydration of ethyl alcohol at active aluminum oxide and was purified by continual freezing out and filtration through active charcoal. Oxygen was prepared by the decomposition of potassium permanganate that had been recrystallized twice; impurities were removed by freezing out.

2. Catalyst

For the investigation a magnesium-chrome catalyst, consisting of a mixture of magnesium chromite with excess magnesium oxide, was chosen. As an additive, sodium silicate was used. The specific surface of the magnesium-chrome catalyst was measured by adsorption of nitrogen at 183°; it was 70 m^2/g. Elovich and coworkers have studied the adsorption isotherms of propene on these catalysts at -23 and -63° over a wide range of pressures (10^{-4} mm Hg-700 mm Hg) by weighing on a McBean quartz balance. The heterogeneity of the surface was analyzed by Roginsky's method, and it was shown that the magnesium-chrome catalyst has a very heterogeneous surface, with a wide variety of sites with respect to molecular heat of sorption. On introducing the additives into the catalyst, the specific surface did not change appreciably.

3. Arrangement of Apparatus and Procedure

The study of the oxidation of ethylene by oxygen was carried out in a static system, represented in Figure 1. From the gas-holder flasks 2, 3, and 4, gas proceeds to the manifold 1 and is admitted through the taps 15 and 16 to the reactor 10. The latter is contained in an electric furnace 11, the p.d. across which is regulated by means of a variable resistance, which is switched in across a stabilizer. The temperature is measured at the wall of the reactor by means of a copper-constantan thermocouple and a potentiometer. The variation in temperature did not usually exceed ±2°. In a number of cases, in order to obtain more accurate measurements, baths containing constant-boiling liquids (ethyl alcohol 78°, toluene 110°, aniline 184°) were used. The upper joint of the reactor was surrounded by solid carbon dioxide to protect the catalyst from the vapor of the

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grease. Water formed in the reaction was frozen out in the trap 12, which was immersed in a Dewar vessel containing solid carbon dioxide. The reaction was followed by the fall in pressure in the McLeod gage 7, joined to the fore-vacuum flask 9.
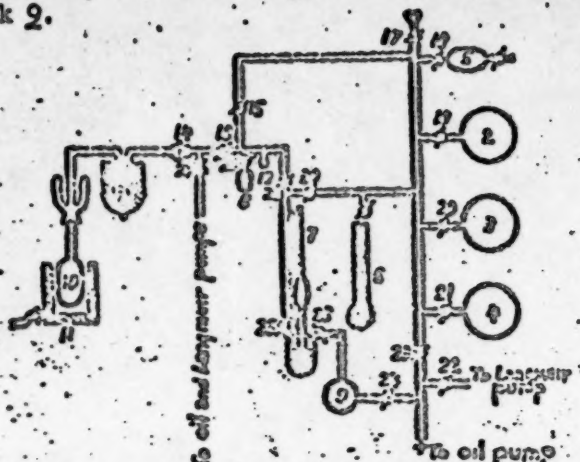
Figure 1. Diagram of apparatus: 2,3,4) gas collectors; 5) calibrated volume; 6) manometer; 7) McLeod gage; 8) absorber containing alkali; 9) fore-vacuum flask; 10) reactor; 11) electric furnace; 12) trap; 13) side-tube for gas analysis; 14) joint; 15-31) taps.

Also, the amount of carbon dioxide formed was measured by absorption by solid caustic alkali in the absorber 8 and by freezing it out in the side tube 13. The procedure was as follows: a weighed amount of catalyst was placed in the reactor (0.02-0.2 g magnesium chromite), protected with the aid of solid carbon dioxide from the vapor of grease, and activated at 450° for 2 hours. The temperature was then brought to that required in the experiment and maintained at that level for one hour. Under identical conditions in absence of catalyst the transfer coefficients of the gases used were determined at various temperatures. Pure ethylene, pure oxygen, or a stoichiometric mixture of these gases was transferred from a definite volume into the reactor, and the kinetics of the oxidation reaction were followed by the change in pressure; the water formed in the reaction was frozen out in the trap, which was surrounded by solid carbon dioxide. At definite intervals the gas mixture was analyzed for its content of carbon dioxide, ethylene, and oxygen.

4. Oxidation of a Stoichiometric Mixture of Ethylene and Oxygen

In Figures 2, 3, and 4, kinetic curves are given for the oxidation of a stoichiometric mixture of ethylene and oxygen. Expressed in coordinates of pressure change (mm Hg) and time t (min.), the curve at first rises steeply and then saturation sets in.

Under static conditions at low pressure, with repeated reaction the oxidation process became slower until it reached a constant condition, which did not change in further experiments. In the oxidation of a mixture of ethylene and air under dynamic conditions, the activity of the magnesium-chrome catalyst remained unaltered for a long period. The lowering of the activity of the catalyst under static conditions may be explained by a reversible or irreversible poisoning of the surface. The filling of the active sites by one of the components of the reaction can lead to a reduction in the rate of reaction. Simultaneously with the catalytic reaction, chemisorption [2] may proceed, and this, according to a number of investigators, is a complex process, leading on the one hand to the activation of the molecules of the reacting substances at the surface, and on the other hand to the non-participation of molecules that are firmly bound to the surface in the reaction; in this latter case, chemisorption becomes a blind alley for the reaction. From this point of view, a detailed analysis of the balance of the reaction makes it possible to separate the processes of chemisorption and of

reaction. It is shown in Table 1 that as reaction is repeated for a stoichiometric mixture the proportion of oxidized ethylene constantly falls and after 5 experiments amounts to only 18%, whereas the proportion of sorbed ethylene on
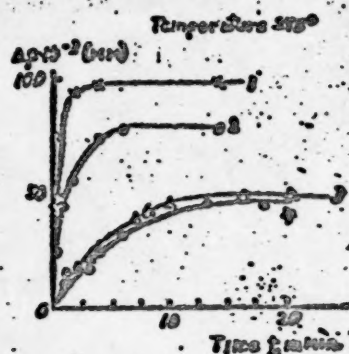
Fig. 2. Dependence of the reaction rate (pressure change) for the oxidation of ethylene at 275° on time; 1, 2, 3 and 4 indicate successive experiments.

Fig. 3. Dependence of the reaction rate for the oxidation of ethylene at 320° on time; 1, 2, 3, 4 as before.

the surface of the catalyst rises from experiment to experiment and attains 60%. The fall in the overall rate (see Figures 2 and 3) and the attainment of a so-called "stationary" state are deceptive, for under these conditions ethylene scarcely undergoes oxidation and only blocks the surface of the catalyst. Simultaneously with the sorption of ethylene, sorption of oxygen, which does not react with the ethylene, occurs. At the same time it should be noted that the proportion of unused ethylene (residue) remains constant, i.e., the surface is not saturated with sorbed hydrocarbon, whereas the proportion of unused oxygen increases from experiment to experiment and attains 20%. In other words, either the activation energy for the sorption of ethylene is considerably greater than that for oxygen so that the process is determined by the sorption of ethylene, or they are sorbed at different sites, and the proportion of adsorption sites for oxygen is considerably less than for ethylene.

Fig. 4. Dependence of the reaction rate for the oxidation of ethylene at 380° on the time.

It is possible that in addition to sorption the process of the dissolution of oxygen in the catalyst may occur. The "poisoned surface" may be regenerated by reaction with oxygen in the gas phase (Experiment 6, Table 1); the surface ethylene is burned out, and the activity of the catalyst is practically fully regained.

When the reaction is carried out in a gas stream with excess of oxygen, regeneration of the catalyst surface by oxygen is occurring constantly, and therefore the activity of the catalyst does not alter over a long period. Change

TABLE 1

Reaction Balance for the Oxidation of a Stoichiometric Mixture of Ethylene and Oxygen

Experiment No.	Initial pressure of the stoichiometric mixture p_0 (mm Hg)	Ethylene (%)			Oxygen (%)		
		Oxidized	Sorbed on surface	Residue	Oxidized	Sorbed on surface	Residue
1	0.182	79.5	14.3	5.5	79.5	14.5	5.5
2	0.172	70.0	26.3	3.7	70.0	20.8	8.2
3	0.172	62.8	32.6	4.6	62.8	23.8	13.4
4	0.172	53.2	42.2	2.1	53.2	27.3	19.5
5	0.172	18.6	60.6	1.6	18.6	51.3	20.1
		Oxygen at 99 mm Hg admitted					
6	0.163	78.0	21.0	0.5	78.0	20.5	0.5

in the activity of the catalyst would no doubt occur in catalytic oxidation reactions with less than the stoichiometric proportion of oxygen. Analogous changes in the surface have been observed by Elovich and coworkers in a study of the oxidation of CO at MnO_2 [2].

The process is expressed by the following kinetic equation:

$$\frac{dq}{dt} = ac^{-\alpha q}(q_0 - q), \qquad (1)$$

where q is the amount of reacting substance, α and a are constants, and t is the time. The coefficient α is a measure of the heterogeneity of the surface with respect to energy. As the process is continued, and therefore also chemisorption, the surface becomes leveled out and more homogeneous, and the kinetic equation goes over into a unimolecular one:

$$w = k(q_0 - q). \qquad (2)$$

In the oxidation of ethylene at a magnesium-chrome catalyst, the same kinetic law is observed, and the surface changes as the reaction is continued. In Figure 5, the transition of the reaction over to the unimolecular law is shown. On introducing an additive (sodium silicate) into the magnesium-chrome catalyst, the equation for the oxidation reaction of ethylene, both under dynamic conditions at atmospheric pressure and under static conditions at low pressure, is not affected.

In Figure 6, results are shown for the oxidation of ethylene at a catalyst containing various amounts of additive. If the reaction rate equation is as follows

$$w = w_0 e^{-\alpha \Delta p}, \qquad (3)$$

where w_0 is the initial rate, α is a coefficient, and Δp is the change in pressure resulting from reaction in mm, then

$$\frac{1}{2,3}\alpha \Delta p = \log \alpha w_0 + \log \left(t + \frac{1}{\alpha w_0} \right)$$

When this equation is written for two experimental points and one is divided by the other [4] we obtain

$$\frac{\log (1 + \alpha w_0 t_1)}{\log (1 + \alpha w_0 t_2)} = \frac{\Delta p_1}{\Delta p_2} .$$

By choosing the two points so that

$$\frac{\Delta p_1}{\Delta p_2} = 2$$
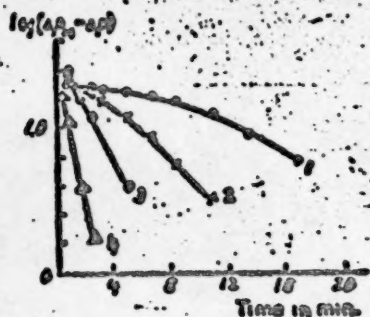
Fig. 5. Kinetic curves for the oxidation of ethylene: 1,2,3,and 4 indicate successive experiments
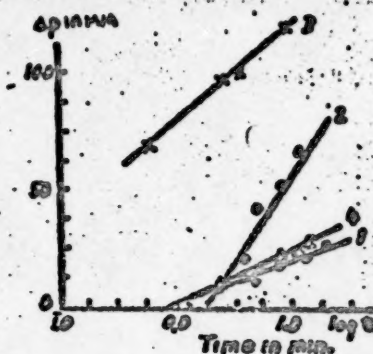
Fig. 6. Dependence of the rate of oxidation reaction of a stoichiometric mixture of ethylene and oxygen at various catalysts at 320° on the log of time: 1) magnesium-chrome catalyst, 2) magnesium-chrome + 1% sodium silicate, 3) magnesium-chrome + 2% sodium silicate, 4) magnesium-chrome + 3% sodium silicate
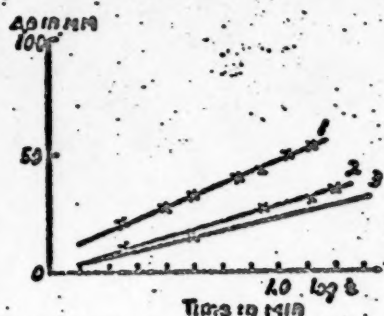
Fig. 7. Dependence of the reaction rate of the oxidation of ethylene at 300° for different catalysts at stationary activity on the log of the time: 1) magnesium-chrome catalyst, 2) magnesium-chrome + 1% sodium silicate, 3) magnesium-chrome + 2% sodium silicate, 4) magnesium-chrome + 3% sodium silicate
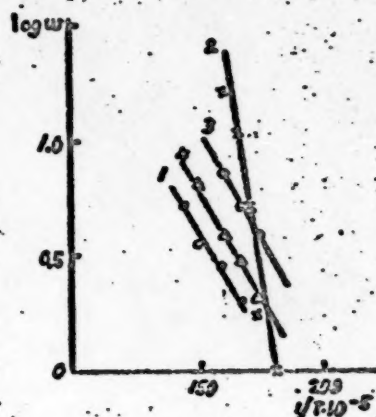
Fig. 8. Dependence of the log of the initial reaction rate of oxidation at a surface in the "stationary" state on $1/T$ for different catalysts: 1) magnesium-chrome catalyst, 2) magnesium-chrome + 1% sodium silicate, 3) magnesium-chrome + 2% sodium silicate, 4) magnesium-chrome + 3% sodium silicate

we obtain

$$\alpha w_0 = \frac{t_2 - 2t_1}{t_1^2}$$

where t_2 and t_1 are the times, w_0 is the initial rate, and α is a coefficient.

The coefficient α is calculated from the following equation

$$\alpha = \frac{2.3 \left[\log\left(t_1 + \frac{1}{\alpha w_0}\right) - \log\left(t_2 + \frac{1}{\alpha w_0}\right)\right]}{\Delta p},$$

where Δp is the change in pressure resulting from the reaction.

The values of the initial rates and heterogeneity coefficients α for the various catalysts are given in Table 2.

As will be seen from the table, the initial rate, which corresponds to maximum activity, varies by a factor of 100. On introducing the additive, the coefficient α at first falls very sharply, and then rises slowly It is interesting to note that variation in the content of additive evidently leads to variation in the extent to which chemisorption participates in the reaction of the oxidation of ethylene. In Figure 7 are given the results of the oxidation of ethylene at catalysts with various contents of additive in the so-called "stationary state" of activity (Figures 2 and 3). Even with such a change of surface, the initial rate and α depend on the amount of additive.

TABLE 2

Initial Reaction Rates for the Oxidation of Ethylene and Heterogeneity Coefficients for Various Catalysts

Catalyst	Initial rate (mm/min)	Heterogeneity coefficient α (mm^{-1})
Pure Mg – Cr	9.7	0.120
Mg–Cr + 1% SiO_2	9.3	0.010
Mg–Cr + 2% SiO_2	1058.0	0.050
Mg–Cr + 3% SiO_2	8.9	0.075

If the activation energy and pre-exponential factor are calculated from the initial rates, then, as will be seen from Figures 8 and 9, the same sort of curve with a sharp maximum is obtained as was found for the oxidation of ethylene at catalysts with additives under dynamic conditions at atmospheric pressure The value of the activation energy varies by a factor of four with variation in the content of additive in the catalyst.

SUMMARY

1. A study has been made of the oxidation reaction of ethylene at a magnesium-chrome catalyst with an addition of sodium silicate under static conditions under a pressure of up to 2 mm Hg.

2. It is shown that the activity of the catalyst varies owing to the simultaneous occurrence of two processes – oxidation and sorption of a component.

3. The activity of the catalyst is restored by treatment of the surface with oxygen.

4 Under dynamic conditions with a great excess of oxygen, the surface is continuously regenerated, and the activity of the catalyst remains unaltered over a long period.

5. In the oxidation of ethylene under static conditions at catalysts with additives, the characteristic peculiarities of the modification phenomenon, which we observed in our earlier dynamic experiments, were observed again.

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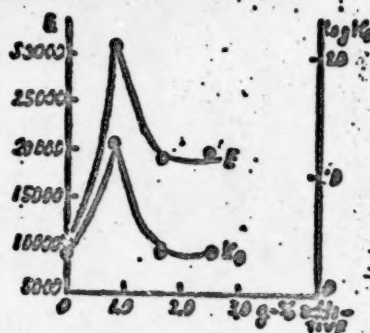
Fig. 9. Dependence of the activation energy and the logarithm of the pre-exponential factor on the content of additive for the oxidation of ethylene at catalysts in the "stationary state" of activity.

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THE THEORY OF CHROMATOGRAPHY ON HETEROGENEOUS SURFACES

COMMUNICATION 1. DETERMINATION FROM DESORPTION CURVES OF THE FUNCTION
EXPRESSING THE DISTRIBUTION WITH RESPECT TO THEIR HEATS
OF ADSORPTION OF SITES ON A SOLID SURFACE

S. Z. Roginsky and M. I. Yanovsky

Recent work has shown clearly that it is impossible to base the theory
of the adsorption of individual substances and mixtures on concepts that relate
to a homogeneous surface. The development of the statistical theory of ad-
sorption phenomena, which takes into account the presence on a solid surface
of sites with widely varying adsorption and kinetic coefficients, has enabled
these difficulties to be largely eliminated. For low and medium site-occupa-
tion, the theory of heterogeneous surfaces is in good agreement with experi-
mental results [1].

The theory of chromatographic separation processes, which were first
discovered by Tsvet [2], can be constructed only with a knowledge of the
adsorption statistics; hence, in working out the theoretical basis of sep-
aration by adsorption it is necessary to take the results of statistical
theory into account. This is particularly important in the region of low
site-occupation.

As statistical analysis of the adsorption equilibria of individual
substances shows, the character of the isotherms is determined by the so-
called distribution functions $\rho(Q)$, expressing distribution with respect to
heats of adsorption of sites on the surface. For the adsorption of mixtures,
the character of the adsorption equilibrium at a heterogeneous surface is
determined by the form of the functional relationship between the heats of
adsorption of the components of the mixture at the same sites [3], as well
as by $\rho(Q)$. In the present work, the possibility of applying relatively
simple chromatographic measurements to the determination of the distribu-
tion function $\rho(Q)$ has been investigated.

According to statistical theory, the process occurring at an active
surface is the overall result of the summation of a number of independent
processes occurring on different sites. In many cases, summation may be
replaced by integration. If, for example, any property $F(x)$ of the surface
S depends on the variable x, then, for a surface that is not homogeneous
with respect to $\underline{x}$, the value of the property $F(x)$ is expressed by the
following integral [4]:

$$F(x) = \int_{x_1}^{x_2} f(x)\, \rho(x) \cdot dx. \tag{1}$$

Here $\rho(x)$ is the distribution function for the surface $\underline{S}$ with respect to
the variable $\underline{x}$, or in other words, $\rho(x)$ is the "statistical weight" of
sites having a given value of $\underline{x}$, i.e.,

$$\rho(x) = \frac{dS(x)}{dx},$$

$f(x)$ gives the dependence of F, the property studied, on x for a homogeneous surface.

Knowing $\rho(x)$, $F(x)$ can be calculated for a heterogeneous surface, and, on the other hand, knowing the law expressed by $F(x)$, the distribution function $\rho(x)$ may be found.

With regard to the application of this to adsorption equilibria, an interesting integral property of a heterogeneous surface is the amount of adsorbed substance as a function of the concentration $\phi(c)$. The heat of adsorption Q on separate sites on the surface is chosen as variable. Replacing x by Q in the integral of Equation 1, we obtain:

$$\Phi(c) = \int_{Q_1}^{Q_2} f(c)\rho(Q)dQ. \tag{2}$$

Here $f(c)$ represents the isotherm for adsorption on a homogeneous surface; it is in its turn a function of the heat of adsorption Q. $\rho(Q)$ is the distribution function of surface sites with respect to heats of adsorption Q. $Q_2 - Q_1$ is the interval over which the heats of adsorption vary. The strict solution of the integral of Equation 2 generally presents considerable mathematical difficulties [5], but, as one of us has shown [1], when the interval over which the heats of adsorption vary is sufficiently wide, the solution of the integral of Equation 2 may be often replaced with sufficient accuracy by the solution of the simpler integral:

$$\Phi(c) \approx \int_{Q_n = RT \ln \frac{b_0}{c}}^{Q_{max}} \rho(Q)dQ \tag{3}$$

Here b_0 is a constant in the equation for the desorption factor in Langmuir's isotherm.

$$b = b_0 e^{-Q/RT}.$$

From Equation 3 a simple method can be found for determining the distribution function $\rho(Q)$ from a given adsorption isotherm $\Phi(c)$ for a heterogeneous surface. For this purpose it is sufficient to integrate Equation 3 for the lower limit:

$$\rho(Q) = \frac{1}{RT} \frac{d\Phi(c)}{d\ln c} \tag{4}$$

Equation 4 permits a direct graphical treatment of the experimental isotherm $\Phi(c)$ without previously determining its analytical expression. For this purpose it is sufficient to plot the experimental points in the co-ordinates $\Phi(c)$ – $\ln c$ and to perform graphical differentiation. Concrete examples of the analysis of experimental results on adsorption equilibria

with the aid of Equation 4 are given in a special monograph [1].

In chromatographic practice, the determination of adsorption isotherms in the region of low saturation may present considerable difficulties. In such cases, Equation 4 cannot be used for determining $\rho(Q)$. However, owing to a definite resemblance of Equation 4 to the generally known fundamental equation of chromatography [6] the function $\rho(Q)$ can be readily determined from the desorption curves. The essence of the proposed method lies in the following. The fundamental equation of chromatography [6] gives the following simple relationship between the main parameters of the chromatographic process:

$$\frac{V}{x} = M\frac{d\Phi(c)}{dc} = M\Phi'(c) \tag{5}$$

or

$$\Phi'(c) = \frac{1}{M} \cdot \frac{V}{x} \tag{5a}$$

Here, $\underline{V}$ is the volume of the solution that has passed; $\underline{x}$ is the distance from the beginning of the column, measured in the direction of flow; $\underline{c} = \underline{c}(x,V)$, the variable concentration of the substance being sorbed in the column; $\Phi(c)$ is the value of the adsorption isotherm at concentration $\underline{c}$; $\underline{M}$ is the weight of a linear cm of charge, when the column is of constant cross-section.

As is well known, Equation 5 is applicable both to adsorption and to desorption of the substance. When a slow stream (concentration of sorbate — $\underline{c}$) passes through a layer of carefully ground adsorbent, a sharp "front" is formed. To the left of the front, the sorbent is saturated up to the value $\Phi(c_0)$, determined by the initial concentration c_0. To the right of the front, the sorbent is completely free from sorbate. Thus, for adsorption from a stream, Equation 5 leads to Shilov's model [7] with an infinitely thin "working layer", which, in absence of "wall" effects and "protuberances" [8], lies perpendicular to the direction of flow. Strictly speaking, Equation 5 is correct only when adsorption equilibrium is established instantaneously in the layer and when longitudinal diffusion can be neglected in comparison with the transfer of substance by the moving stream. Of considerably greater interest is the use of Equation 5 for the dynamic desorption of a substance from a layer by a non-sorbable gaseous or liquid carrier. As already shown [9], in this case the fore-front of the sorbed substance moves forward through the layer without changing its sharpness, and the hind-front is gradually drawn out, its form and magnitude being determined by the form of the adsorption isotherm.

Combining Equations 4 and 5, we may greatly simplify the problem of determining $\rho(Q)$. For this purpose we shall write Equation 4 in the following form:

$$\rho(Q) = \frac{d\Phi(c)}{RT\,d\ln c} = \frac{c}{RT}\frac{d\Phi(c)}{dc} = \frac{c}{RT}\Phi'(c)$$

Substituting in Equation 4 the value of $\Phi'(c)$ from Equation 5a, we obtain:

$$\rho(Q) = \frac{cV}{MxRT} \tag{6}$$

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By using Equation 6, the problem of determining $\rho(Q)$ amounts only to the standard chromatographic measurement of the desorption curve $c = c(x,V)$ giving the relation between the concentration c of the substance in the liquid or gaseous carrier after passing through a sorbent layer of length x and the amount V of pure carrier entering the column during this time.

In Fig. 1, a typical desorption curve is represented diagrammatically. This curve will be described by Equation 5 if, in addition to the conditions indicated above, the following conditions are observed:

1) dynamic desorption is carried out by a non-sorbing carrier;

2) the adsorption isotherm is convex to the axis of ordinates and has no points of inflection.

In its first part, the desorption curve ABCD is characterized by the presence of the horizontal section AB at a distance of $c = c_0$ from the V-axis, where c_0 is the initial concentration of the adsorbate at which the layer becomes saturated. Beyond the horizontal section there is at first a fairly sharp fall in the effluent concentration, but later the rate of fall dc/dV diminishes considerably, particularly in regions of low concentration. It will be seen from Fig. 1 that the distribution function $\rho(Q)$, defined by Equation 6, is proportional to the area OGCE, which is shaded in the figure, and inversely proportional to the product MxRT:

$$\rho(Q) = \frac{\text{area OGCE}}{\text{MxRT}} \tag{6a}$$

The falling portion of the desorption curve yields a simple method for constructing the graph of the function $\rho(Q)$. For this purpose, the value of $RT \ln c$ is taken as abscissa (it is proportional to the heat of adsorption Q), and the value of Vc, proportional to the distribution function $\rho(Q)$, is taken as ordinate (Fig. 2).
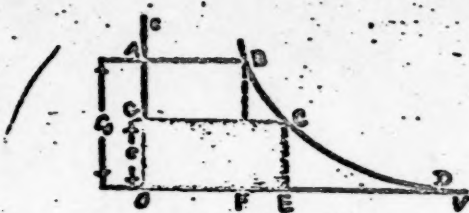
Fig.1. Determination of the distribution function with respect to heats of adsorption for sites on the surface

$$\rho(Q) = \frac{\text{area OGCE}}{\text{MxRT}}$$

Fig. 2. Construction of the graph for $\rho(Q)$ in accordance with the desorption curve $c = c(V)$.

Thus, when we have the desorption curve $c = c(V)$, we may construct the graph $\rho = \rho(Q)$ without having recourse to adsorption measurements.

If the equation of the desorption curve $c = c(V)$ is given in explicit form, then, in accordance with Equation 6, there is no difficulty in determining $\rho(Q)$; and, on the other hand, if the function $\rho(Q)$ is known,

then it is easy to find the desorption curve $\underline{c} = \underline{c}(V)$. Let us examine, for example, the frequently occurring case of distribution in accordance with a power law:

$$\rho = HQ^n \tag{7}$$

Substituting $\rho(Q)$ in quation 6 by its value from Equation 7, and replacing Q by $RT \ln \frac{b_0}{c}$, we obtain, after elementary rearrangement:

$$\frac{c}{\left(\ln \frac{b_0}{c}\right)^n} = \frac{HM x (RT)^{1+n}}{V} \tag{8}$$

Equation 8 is the general equation of desorption curves for distributions according to a power law. For exponential distribution

$$\rho = He^{-\alpha Q} \tag{9}$$

where α is the coefficient of non-uniformity, and we have

$$\alpha = (nRT)^{-1}$$

and

$$H = \frac{ab_0^{1/n}}{n \cdot RT} \,;$$

In an analogous manner we obtain the following equation for the desorption curve:

$$c = \frac{(HM x RT)^{1/1+\alpha RT} \cdot b_0^{\alpha/RT(1+\alpha RT)}}{V^{1/1-\alpha RT}}. \tag{10}$$

It is interesting to note that when α and $\underline{n}$ tend to zero, both the exponential and the power distributions go over into a uniform distribution:

$$\rho = H. \tag{11}$$

for which the equation of the desorption curve takes up the following simple hyperbolic form:

$$c = \frac{HM x RT}{V}. \tag{12}$$

It should be emphasized that over short ranges the exponential distribution is often indistinguishable from the power distribution, and hence conclusions concerning the character of the distribution made from the desorption curve may be made only when the range of measured concentrations is sufficiently wide.

SUMMARY

1. The effect of energetic inhomogeneity of the surface on the character of the dynamic desorption curves in chromatographic analysis has been analyzed.

2. The relation between the form of desorption curves $\underline{c} = \underline{c}(V)$ and the form of the function expressing the distribution with respect to their heats of adsorption of sites on the surface $\rho(Q)$ has been obtained.

3. A method is given for the construction of $\rho(Q)$ from desorption curves without having recourse to special adsorption measurements.

4. The equations of desorption curves for the fundamental forms of distribution are obtained.

5. The limits and conditions of applicability of the proposed method are pointed out.

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THE THEORY OF CHROMATOGRAPHY ON HETEROGENEOUS SURFACES.

COMMUNICATION 3. DYNAMICS OF THE ADSORPTION OF MIXTURES ON HETEROGENEOUS SURFACES

S. Z. Roginsky and M. I. Yanovsky

The dynamics of the adsorption of mixtures for medium degrees of saturation have been studied in a number of investigations [1,2,3]. The theoretical concepts of this field have recently been applied to chromatographic adsorption analysis, which was discovered by Tsvet [4]. At the basis of the so-called " chromatographic frontal analysis" lies the application of the Shilov-Dubinin [6] "parallel transfer" principle to the case of the adsorption of mixtures that conform to Langmuir's equation, which is typical for energetically homogeneous surfaces.

The assumption of the energetic homogeneity of the surface of the adsorbent does not generally lead to great complications for medium degrees of saturation, inasmuch as the Langmuir equation is a sufficiently good interpolation formula in this region. The picture changes sharply when we go over to a low total saturation, for it is then impossible to have only medium saturation θ and medium desorption coefficients b for all the surfaces of the adsorbent.

The recent development of the statistical theory of adsorption [7] and the extension of the conclusions from this theory to the adsorption of mixtures [8] permits the dynamics of the adsorption of mixtures at low saturation to be analyzed in greater detail.

In the present work, which is based on the conclusion of statistical theory [7,8], an attempt is made to expose the typical peculiarities of the dynamics of the adsorption of mixtures at a heterogeneous surface.

Adsorption Equilibrium

In accordance with statistical theory, the character of the adsorption equilibrium of a mixture of two substances at a heterogeneous surface is determined by the form of the functional relation between the heats of adsorption Q_1 and Q_2 of the components of the mixture on one type of site:

$$Q_2 = \varphi(Q_1). \tag{1}$$

As we cannot go into detail concerning the dependence of this functional relationship on the nature of the adsorption forces, we will point out only the probability of the existence of three fundamental cases: a symbathic relationship, an antisymbathic relationship, and absence of any relationship between the heats of adsorption of the components.

From the point of view of the practical chromatographic separation of liquid organic mixtures and gases, the case of a symbathic relationship between the heats of adsorption is the most interesting. Such a relationship is to be expected, in particular, for all cases of adsorption that

result mainly from the operation of dispersion forces, e.g., in the adsorption of mixtures of aliphatic hydrocarbons, of mixtures of inert gases, etc , when chromatographic separation, owing to the closeness of the adsorption coefficients, meets with particularly great difficulty. The simplest example of the symbathic change of Q_1 and Q_2 is the case of direct proportionality between the heats of adsorption:

$$Q_2 = \beta Q_1. \tag{2}$$

In the present work, we are confining ourselves to the analysis of this one simple case, which is often met in practice.

In Fig. 1 is shown the graph used in statistical theory [8] for analyzing the equilibrium of a mixture of two substances. Along the axis of abscissas, the heat of adsorption of one of the components, e.g., Q_1, is given, and along the other axis — the following quantities:

$\rho(Q)$, the function expressing the distribution with respect to their heats of adsorption Q_1 of sites on the surface. This quantity is determined by the fraction of the surface occupied by sites having heats of adsorption lying within the limits Q_1 to $Q_1 + dQ_1$.

b_1, the desorption coefficient of the first substance.

b_2, the desorption coefficient of the second substance.

The relations between the desorption coefficients and the heat of adsorption are given by the following equations:

Fig. 1. Initial graph for the analysis of the adsorption equilibria of a mixture of two substances.

$$b_1 = b_{01}e^{-Q/RT} \tag{3}$$

and

$$b_2 = b_{02}e^{-Q/RT} \tag{3a}$$

The desorption coefficients b_1 and b_2 are numerically equal to the concentrations c_1 and c_2 at which, in absence of other substances, half the surface is occupied ($\theta = 0.5$). Hence, along the ordinate axis in Fig. 1, we may give also values of the concentrations c_1 and c_2. It follows from the above that from the intersections of the $b_1(Q_1)$ and $b_2(Q_1)$ with the straight lines $c_1 = $ const. and $c_2 = $ const. we may determine the heats of adsorption Q'_1 and Q'_2 of the corresponding groups of sites on the surface of the adsorbent, half of which is filled by sorbate. In view of the steep exponential relationship between the saturation θ and the heat of adsorption Q, it may be assumed that on the distribution graph $\rho(Q)$, to the left of Q_1 ($b_1 > c_1$) the surface is practically free from the first substance ($\theta_1 \approx 0$), and to the right of Q_1 ($b_1 < c_1$) it is fully occupied ($\theta \approx 1$). Analogous considerations apply for substance 2:

to the left of Q''_1 ($b_2 > c_2$) and $\theta_2 \approx 0$,

to the right of Q''_1 ($b_2 < c_2$) and $\theta_2 \approx 1$.

When adsorption from a mixture is characterized by a fight for the surface, the ratio of the fractions of the surface occupied by the components will be determined by the ratios c_1/b_1 and c_2/b_2:

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$$\Delta = \frac{\theta_2}{\theta_1} = \frac{c_2}{c_1}\frac{b_1}{b_2} = \frac{c_2}{c_1}\frac{b_{01}}{b_{02}} e^{\frac{(\beta-1)Q_1}{RT}} \qquad (4)$$

From Equation 4 it will be seen that there is a possibility of a considerable preponderance of one of the gases on certain sites of the surface and even over the whole surface.

This is shown in Fig. 2, in which there are plotted as abscissas not only b_1, b_2, c_1, c_2, and $\rho(Q)$, but also the ratio b_2/b_1 of the desorption coefficients and the concentration ratio c_2/c_1. The abscissa Q_1° of the intersection of the straight line c_2/c_1 = const. with the curve $b_2/b_1(Q_1)$ is the limit to the left of which the surface is practically completely occupied by substance 1 and to the right of which — by substance 2. Analytically, Q_1° is found from the equation:

Fig. 2. Determination of the distribution of two substances when the heats of adsorption are symbathically related

$$Q_1^\circ = \frac{RT}{\beta-1} \ln \frac{c_1}{c_2}\frac{b_{01}}{b_{02}}. \qquad (5)$$

The ordinate c_1^* of the point of intersection of the straight line Q_1° = const. with the curve $b_1(Q_1)$ permits calculation of the extent of the adsorption of the components on the basis of the adsorption isotherms of the pure substances:

$$\underline{f}_1(c_1 c_2) = \int_{Q_1'}^{Q_1^*} \rho(Q)dQ =$$

$$= \int_{Q_1'}^{Q_{max}} \rho(Q)dQ_1 - \int_{Q^*}^{Q_{max}} \rho(Q)dQ = \underline{f}_1(c_1) - \underline{f}_1(c_1^*). \qquad (6)$$

$$\underline{f}_2(c_1 c_2) = \int_{Q_1^*}^{Q_{max}} \rho(Q)dQ = \underline{f}_1(c_1^*). \qquad (7)$$

The value of c_1^* may be found, also analytically, from the equation:

$$c_1^* = b_{01}e^{-Q^*/RT} = b_{01}(c_2/c_1 \cdot b_{01}/b_{02})^{1/\beta-1} \qquad (8)$$

Dynamics of Adsorption

We will examine the movement of the mixture through a layer of adsorbent, assuming instantaneous establishment of equilibrium at each point of the layer and neglecting the effect of diffusion along the direction of the stream in comparison with the velocity of the stream. This leads to the diagram shown in Fig. 3 [1,2,3].

Two sorption waves move through the layer. The first substance, which is sorbed less readily than the second, moves with the greater velocity. The movement of the adsorption wave of the more readily sorbing substance 2 is accompanied by partial desorption of the less readily sorbing substance 1, and, for this reason, the concentration c'_1 of this substance in the first wave is higher than the influx concentration c_1^0. The distribution of adsorbed substances corresponding to Fig. 3 is shown diagrammatically in Fig. 4. Separate sections of the distribution curve and also the concentration c'_1 of

substance 1 in the first sorption wave can be calculated for the case of symbathically related heats of adsorption in the following manner. We start from the adsorption isotherms for the components of the mixture (Equations 6 and 7).

We will suppose that a certain volume V_0 of gaseous carrier containing the sorbates in concentration c_1 and c_2^0 is passed through the charge. The width x_2 of the zone in which both substances are adsorbed is determined by the following obvious relationship, which is valid so long as the amount of substance contained in the space not occupied by adsorbent is neglected:

$$\frac{V_0}{x_2} = \frac{f_2\,(c_1^0,\ c_2^0)}{c_2^0} \tag{9}$$
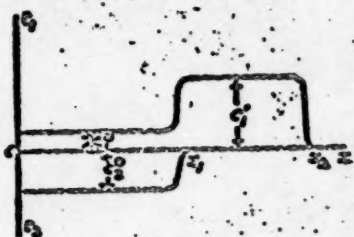
Fig.3. Distribution of concentrations along the length of the layer (adsorption dynamics of a mixture of two substances for $c_2 \ll c_1$)
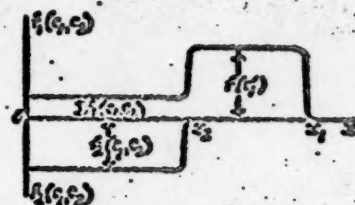
Fig.4. Distribution of the adsorbed substances over the length of the layer for $c_2 \ll c_1$

Substituting $f_2'(c_1,c_2)$ by its value from Equation 7, we obtain

$$x_2 = \frac{V_0 c_2^0}{f_1(c_1^0)} \tag{9a}$$

The quantity m_{1x_2} of substance 1 sorbed in the layer x_2 is found in the following manner:

$$m_{1x_2} = f_1(c_1^0,\ c_2^0) \tag{9b}$$

We substitute the value of $f_1(c_1^0, c_2^0)$ from Equation 6 and the value of x_2 from equation 9a in equation 9b:

$$m_{1x_2} = \frac{V_0 c_2^0}{f_1(c_1^*)}\ [f_1(c_1^0) - f_1(c_1^*)]. \tag{9c}$$

The quantity $m_{1x_1x_2}$ of substance 1 adsorbed in the first sorption wave is determined by taking the difference between the total amount m_1 entering the layer in volume V_0 and the amount m_{1x_2} adsorbed on the section x_2:

$$m_{1x_1x_2} = m_1 - m_{1x_2} = V_0 c_1^0 - \frac{V_0 c_2^0}{f_1(c_1^*)}\cdot[f_1(c_1^0) - f(c_1^*)]. \tag{9d}$$

Hence we can define the width of the zone $x_{1,2}$ in which only substance 1 is adsorbed without admixture of substance 2:

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$$x_{1,2} = \frac{m_1 x_1, x_2}{f_1(c_1^1)} = \frac{V_0 c_1^0}{f_1(c_1^1)} - \frac{V_0 \cdot c_2^0}{f_1(c_1^1)} \left[\frac{f_1(c_1^0) - f_1(c_1^*)}{f_1(c_1^1)} \right], \qquad (9e)$$

Here, $f_1(c_1^1)$ represents the adsorption of substance 1 in the first adsorption wave — corresponding to concentration c_1^1. The width of the zone x_1 is given by the sum of x_2 and $x_{1,2}$:

$$x_1 = x_2 + x_{1,2}.$$

or, in accordance with Equations 9a and 9e:

$$x_1 = \frac{V_0 c_2^0}{f_1(c_1^1)} + \frac{V_0 c_2^0}{f(c_1^1)} \frac{f(c_1^0) - f_1(c_1^*)}{f_1(c_1^1)}. \qquad (9f)$$

On the other hand, for the rate of movement of the first sorption wave we may write the following relationship:

$$\frac{V_0}{x_1} = \frac{f_1(c_1)}{c_1^1}$$

whence

$$x_1 = \frac{V_0 c_1^1}{f_1(c_1^1)} \qquad (9g)$$

Equating the R.H.S. of 9f and 9g we obtain the following equation for the concentration c_1^1 of the less readily sorbing substance 1 in the first adsorption wave:

$$c_1^1 = c_1^0 + c_2^0 + \frac{f_1(c_1^1) - f_1(c_1^0)}{f_1(c_1^1)} \cdot c_2^0, \qquad (10)$$

or, in a somewhat modified form,

$$c_1^1 = c_1^0 + \left[1 + \frac{f_1(c_1^1) - f_1(c_1^0)}{f_1(c_1^1)} \right]. \qquad (10a)$$

From Equation 10 it will be seen that the concentration c_1^1 of substance 1 in the first wave is greater than the sum of the influx concentrations $c_1^0 + c_2^0$. If we write

$$1 + \frac{f_1(c_1^1) - f_1(c_1^0)}{f_1(c_1)} = \alpha, \qquad (11)$$

we obtain Yankovsky's formula:

$$c_1^1 = c_1^0 + \alpha c_2^0. \qquad (12)$$

The quantity α is the so-called coefficient of displacement of the first, less readily sorbing substance by the second from the surface of the adsorbent. Below, we shall show the effect of external parameters (total concentration $c = c_1^0 + c_2^0$ ratio of initial concentrations c_2^0/c_1^0 and temperature T) on the value of the displacement coefficient.
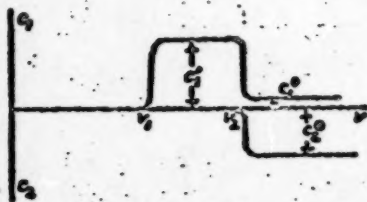
For the case considered, Fig. 5 shows the "effluent curve", which gives the relation between the volume V of the carrier that is passed through and the effluent concentrations c_1^0 and c_2^0. The value V_1 on this curve, which corresponds

Fig. 5. Effluent curve (adsorption dynamics of a mixture of two substances for $c_2 \ll c_1$)

to the volume for which a layer of length x has "worked off" the first, less readily sorbing substance, may be determined from equations 9f and 9g by replacing V by V_1 and x_1 by x:

$$V_1 = \frac{x}{\frac{c_2^0}{f_1(c_1^x)} + \frac{c_1^0}{f_1(c_1^x)} + \frac{c_1}{f_1(c_1^x)} \cdot \frac{f_1(c_1^0) - f_1(c_0)}{f_1(c_1^x)}} \quad (13)$$

or

$$V_1 = x \Bigg/ \frac{c_1}{f_1(c_1^x)} \quad (13a)$$

The value V_2 on the effluent curve (Fig. 5), which corresponds to the passage of the second, more readily adsorbed substance beyond the layer x, can be calculated from Equation 9a by replacing x_2 by x:

$$V_2 = \frac{x}{\frac{c_2^0}{f_0(c_1^x)}} \quad (14)$$

We will now examine in greater detail the effect of external parameters on the dynamics of adsorption.

Effect of the Sum of the Influx Concentrations $c_1 = c_1^0 + c_2^0$

Let us turn again to the initial graph (Fig.1). From this graph it follows that the character of the adsorption isotherm depends greatly on the relative disposition of the limits Q_1^1 and Q_1^*. So long as the composition of the original mixture does not change, the limit Q_1^* also remains unchanged. As the total concentration is diminished, with $c_2^0/c_1^0 = \text{const}$, the region occupied by the first gas will be gradually diminished. When the mixture is diluted c_1^0/c_1 times, where c_1^* is determined by Equation 8, the first substance practically ceases to be adsorbed, and only substance 2 will be on the surface of the adsorbent, consequently:

$$f_1(c_1^0, c_2^0) = 0 \quad (15)$$

and

$$f_2(c_1^0, c_2^0) = f_2(c_2^0). \quad (15a)$$

The isotherms 15 and 15a lead to the peculiar picture of the dynamics of adsorption represented in Fig. 6.

Two sorption waves move through the layer of sorbent. The less readily sorbing substance 1 is completely absent from the second sorption wave. The movement of this wave is accompanied by complete desorption of the less readily sorbing substance 1, and consequently the concentration c_1^1 of this substance in the first sorption wave may be considerably greater than the original concentration c_1^0. The distribution of sorbed substances over the length of the layer up to the moment when a volume V_0 has been passed through the charge is determined in the following manner: the width x_2 of the zone in which only substance 2 is adsorbed is determined from the equation:
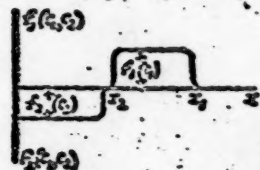
Fig. 6. Distribution of the adsorbed substances over the length of the layer for $c_2 > c_1$

$$\frac{V_0}{x_2} = \frac{f_2(c_2^0, c_1^0)}{c_2^0} \quad (16)$$

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Substituting for $f_2(c_1^0, c_2^0)$ from Equation 15a,

$$x_2 = \frac{V_0 c_2^0}{f_2(c_2^0)} \tag{16a}$$

The region $x_{1,2}$ in which only substance 1 is sorbed is found from the following expression:

$$x_{1,2} = \frac{V_0 c_1^0}{f_1(c_1^1)} \tag{16b}$$

The total length of the layer, x_1, over which substance 1 is removed is given by:

$$x_1 - x_2 + x_{1,2} = \frac{V_0 \cdot c_2^0}{f(c_2^0)} + \frac{V c_1^0}{f_1(c_1^1)} \tag{16c}$$

On the other hand, the velocity of the first sorption wave is evidently given by the equation:

$$V_0/x_1 = f_1(c_1^1)/c_1^1, \tag{16d}$$

whence

$$x_1 = \frac{V_0 \cdot c_1^1}{f_1(c_1^1)} \tag{16e}$$

Equating R.H.S. of Equations 16a and 16c we obtain

$$c_1^1 = c_2^0 + \frac{f_1(c_1^1)}{f_2(c_2^0)} \tag{16f}$$

In this case, the displacement coefficient is defined as the ratio of the amount of substance 1 sorbed per unit length in the first sorption wave to the corresponding value for substance 2 in the second wave:

$$\alpha = \frac{f_1(c_1^1)}{f_2(c_2^0)} \tag{17}$$

The effluent curve then has the form shown in Fig. 7. The value of V_1 on the effluent curve is determined from equations 16f and 16e by replacing V_0 by V_1:

$$V_1 = \frac{x}{c_2^0/f_2(c_2^0) + c_1^0/f_1(c_1^1)} \tag{18}$$

or

$$V_1 = \frac{x}{c_1^1/f_1(c_1^1)} \tag{18a}$$

The value of V_2, which corresponds to the appearance of substance 2 beyond the layer $\underline{x}$ of adsorbent, is determined from Equation 16a by replacing x_2 by x:

$$V_2 = \frac{x}{c_2^0/f_2(c_2^0)} \tag{18b}$$

Combining equations 18b and 18a with 16f we obtain:

$$c_1^0 = c_1^1 \left(1 + \frac{V_1}{V_2}\right) \tag{19}$$

Equation 19 permits the initial concentration c_1^0 to be determined from the concentration c'_1, which is taken from the experimentally found effluent curve. The same curve enables V_1 and V_2 to be determined.

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The ideas we have expressed concerning the effect of the sum of the influx concentrations $c = c_1^0 + c_2^0$ for constant c_2^0/c_1^0 are of fundamental importance for chromatographic practice. In fact, it is quite obvious that it is preferable to work according to the scheme represented in Fig. 6 than according to that of Fig. 4, for in the first case full separation into the components is attained already in the process of "composing" the chromatogram, and there is no need for the complex process of dynamic desorption ("development" of the chromatogram) that is usually applied in chromatography. The following is a practical conclusion arising from these considerations: before proceeding to the dynamic adsorption of a mixture of two substances having initial concentrations of c_1^0 and c_2^0, it is necessary to dilute with an inert carrier by $c_0^0/c_1^0 = \gamma$ times, where c_1^* is determined by Equation 8.

It should be emphasized that owing to the steep exponential form of the relation between the saturation θ and the heat of adsorption Q the transition from scheme 4 to scheme 6 and back is very sudden; the quantity c_1^* is a sort of "critical" factor that completely determines the character of the dynamic adsorption process:

For $c_1^0 > c_1^*$ the adsorption dynamics follow the scheme of Fig. 4;

For $c_1^0 < c_1^*$ the adsorption dynamics follow the scheme of Fig. 6.
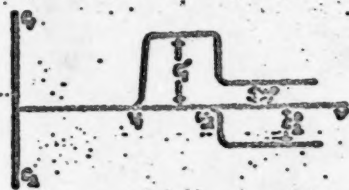
Fig. 7. Effluent curve (adsorption dynamic of a mixture of two substances for $c_2 > c_1$

Effect of the Ratio of Influx Concentrations c_2^0/c_1^0

The relative composition of the mixture c_2^0/c_1^0 determines the position of the internal boundary Q_1^* (Fig. 1). If the influx concentration c_1^0 is constant, then increase in the concentration c_2^0 of the second substance leads to its gradual predominance in the adsorbed phase. At a certain value $(c_2/c_1) = \delta_{crit}$, determined from the equation:

$$\delta_{crit} = (c_2/c_1)_{crit} = \frac{b_{02}}{b_{01}} e^{\frac{Q_1^*(\beta-1)}{RT}}, \tag{4a}$$

the character of the dynamic adsorption process changes sharply:

for $Q_1^* < Q_1'$ the adsorption dynamics follow the scheme of Fig. 6;

for $Q_1^* > Q_1'$ the adsorption dynamics follow the scheme of Fig. 4.

Effect of Temperature T

In agreement with statistical theory [7,8], lowering of temperature moves the curves $b_1(Q_1)$ and $b_2(Q_2)$ downwards and to the left, in the direction of lower values of Q_1. At the same time, the boundaries of Q_1' (Fig. 1), separating the empty from the occupied regions, become sharper. When the concentration c_1^0 of substance 1 is constant, the boundary Q_1 is displaced by an amount that is proportional to the change in temperature:

$$Q_1' = RT \log \frac{b_{01}}{c_1^0} = \text{const } T. \tag{20}$$

The law for the displacement of the internal boundary Q_1 between the two occupied zones is easily obtained by suitable transformation of equation 4a:

$$Q_i = \frac{RT}{\beta - 1} \left[\log \frac{b_{02}}{b_{01}} - \log \left(\frac{c_2}{c_1} \right)_{crit} \right] . \tag{21}$$

It follows from Equation 21 that the logarithm of the critical ratio of concentrations at which the sharp transition occurs from predominance at the adsorbent surface of the first substance to predominance of the second is inversely proportional to the absolute temperature.

In other words, lowering of temperature at constant composition c_2/c_1 leads to a sharp transition from the dynamics scheme of Fig. 4 to the scheme shown in Fig. 6, even when the initial concentration ratio is unfavorable for separation.

Thus, the character of the dynamic process is very sensitive to temperature:

at $T < T_{crit}$, the process goes according to scheme 6,

at $T > T_{crit}$, the process goes according to scheme 4.

The sharp transition from one scheme of dynamic adsorption to another is characteristic only for an energetically heterogeneous surface. It is easy to show that in the case of the adsorption of mixtures that obey Langmuir's equation, which is typical for an energetically homogeneous surface, variations in the total and relative concentrations and in the temperature lead only to a gradual, smooth variation in the relative degrees of saturation of the surface by the components. As is well known, for the adsorption of mixtures according to Langmuir's equation the fractional saturations of substances 1 and 2 are expressed by the equations:

$$\theta_1 = \frac{c_1/b_1}{1 + c_1/b_1 + c_2/b_2} \tag{22a}$$

and

$$\theta_2 = \frac{c_2/b_2}{1 + c_1/b_1 + c_2/b_2} . \tag{22b}$$

For low saturation $c_1/b_1 + c_2/b_2 \ll 1$, and Equations 22a and 22b then lead to

$$\theta_1 = c_1/b_1 \tag{22c}$$

and

$$\theta_2 = c_2/b_2, \tag{22d}$$

i.e. at low saturation the adsorption of the components is not sensitive to the total concentration $c = c_1 + c_2$ and to the relative concentration c_2/c_1. It follows from Equation 22 that the ratio of the fractional saturations of the two components on a homogeneous surface is given by

$$\Delta = \frac{\theta_1}{\theta_2} = \frac{c_1}{c_2} \frac{b_2}{b_1} = \frac{c_1}{c_2} \frac{b_{02}}{b_{01}} e^{\frac{Q_1 - Q_2}{RT}} . \tag{23}$$

Owing to the constancy of the difference $Q_1 - Q_2$, θ_1/θ_2 changes smoothly with change in c_1/c_2, without producing a sudden predominance of one of the components at definite critical values of c_1/c_2. It follows from Equation 22 that change in the temperature T also leads to smooth change in θ_1/θ_2; consequently, the phenomenon of a "critical temperature" (T_{crit}), which is characteristic for a heterogeneous surface, is now absent.

Hence, for a homogeneous surface in the region of low influx concentrations the picture to be expected of the dynamics of the adsorption is that

represented diagrammatically in Fig. 4, according to which fractionation is only partly effected. In a large number of experimental researches into the low-temperature fractional desorption of mixtures of A, Kr, and Xe [9] and of hydrocarbon mixtures [10] the exceptional sensitivity of the separation process to the values of the total and relative concentrations of the components and to the temperature of desorption was established. It was established that for certain total and relative concentrations separation is possible, but for others it is not. Lowering of temperature has a marked effect on the efficiency; above a certain temperature, separation is impossible. These facts, and also the sensitivity that has been remarked in this work of the separation process to the order in which the components are introduced into the adsorption vessel, may be readily explained within the framework of the theory of adsorption at inhomogeneous surfaces.

The problem of the dynamics of the adsorption of mixtures at inhomogeneous surfaces is closely connected with the dynamics of the desorption of mixtures, which play a great role in chromatographic analysis. This question has a special interest of its own and will be examined in another paper.

SUMMARY

On the basis of statistical theory the following results have been obtained:

1. The effect of the heterogeneity of the adsorbent on the dynamics of the adsorption of a mixture of two substances has been investigated.

2. It has been shown that there is a possibility of sudden transitions from one course of dynamic adsorption to another at definite critical values of c, c_1/c_2, and T.

3. The conditions required for complete separation of a binary mixture at a heterogeneous surface have been established.

The ideas that have been brought forward are primarily interesting for the dynamics of the adsorption of mixtures at low saturations of the surface, for which heterogeneity is most strongly marked.

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NEW METHOD OF SYNTHESIZING TRIALKOXYTITANIUM CHLORIDES

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Until recently, the only known compound of the type $(AlkO)_3TiCl$ has been triethoxytitanium chloride, prepared by the action of acetyl chloride on ethyl orthotitanate [1]. We have shown that triethoxytitanium chloride is obtained smoothly by the interaction of equimolecular quantities of pyridine hydrochloride and ethyl orthotitanate in a medium of benzene at 60-70° [2]. This observation permitted us to develop a method of direct synthesis of triethoxytitanium chloride by the reaction of $TiCl_4$ with ethanol in presence of pyridine in benzene medium. At the same time, ethyl orthotitanate and pyridine hydrochloride are formed, and in the subsequent heating of the reaction mixture these form triethoxytitanium chloride according to the equations:

$$4C_2H_5OH + TiCl_4 + 4C_2H_5N \rightarrow (C_2H_5O)_4Ti + 4C_5H_5N \cdot HCl;$$

$$(C_2H_5O)_4Ti + C_5H_5N \cdot HCl \rightarrow (C_2H_5O)_3 TiCl + C_2H_5OH + C_5H_5N$$
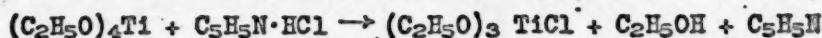
In this way, triethoxytitanium chloride became a readily accessible substance [2]. However, this method does not appear to be a general one; attempts at preparing the triallyloxy- and tri-n-butoxytitanium chlorides and other such compounds were not successful [2]. Only the attempt to prepare tri-n-propoxytitanium chloride by treating n-propyl orthotitanate with pyridine hydrochloride was successful [3].

We considered that it might be possible to prepare trialkoxytitanium chlorides by transesterification (alcoholysis) of the accessible triethoxy compound by the action of alcohols according to the scheme:

$$(C_2H_5O)_3 TiCl + 3ROH \rightleftharpoons (RO)_3 TiCl + 3C_2H_5OH.$$

The replacement of the last Cl in $(C_2H_5O)_3TiCl$ by an alkoxy group by the action of an alcohol must be very difficult, for it is known that in dichlorodialkoxytitaniums the further replacement of chlorine by alkoxy groups by the action of alcohols does not take place even with prolonged heating [1]. The application of the transesterification reaction to triethoxytitanium chloride met with difficulties, for it was found that under the required conditions replacement of chlorine by alkoxy occurs. Since trialkoxytitanium chlorides and alkyl orthotitanates containing the same alkoxy groups boil at similar temperatures, it was not found possible to separate them by distillation. Nevertheless, it was established by special experiments that even in the case of the higher alcohols, which distill off at a higher temperature, the replacement of Cl in $(AlkO)_3TiCl$ by an alkoxy group goes extremely slowly.

Thus, when 10 g of tri-n-hexyloxytitanium chloride is mixed with 50 ml of n-hexyl alcohol and the latter slowly distilled off, then HCl can be detected in the distillate, but even after repeating this procedure ten times, using 500 ml of n-hexyl alcohol, the reaction does not go to completion. If, however, in the above-described experiment triethoxytitanium chloride and ethyl alcohol are taken, then in the first 50 ml of the distillate no trace of HCl can be detected, and with further distillation only traces of chlorine can be detected in the distillate. In contrast with this extremely slow reaction, the transesterification reaction proceeds very rapidly. Hence, by observing definite conditions it was found possible to prepare various trialkoxytitanium

chlorides practically free from contamination with the corresponding alkyl ortho-titanates. These conditions comprise the conducting of the transesterification process at as low a temperature as possible and, in the case of the higher alcohols, also without continual addition of fresh portions of alcohol and, consequently, without their subsequent distillation. According to our observations, a two-fold excess of alcohol, taken at the beginning of the experiment, is sufficient.

The process of transesterification must be watched by making tests on the distillate for chlorine content or by introducing a solution of $AgNO_3$ in absolute alcohol in the receiver prior to the experiment. If HCl makes its appearance in the distillate, it is necessary to carry on distilling off the alcohol in a vacuum at a lower temperature. These precautions are particularly necessary when conducting transesterification with high-boiling alcohols. By this method we have succeeded in preparing the previously unknown tri-n-butoxy-, tri-isobutoxy-, tri-isoamyloxy-, tri-n-hexyloxy-, tri-β-chloroethoxy-, and tri-β-ethoxyethoxy-titanium chlorides.

All the chlorides obtained, with the exception of tri-β-chloroethoxytitanium chloride, are colorless, transparent, viscous, hygroscopic liquids that may be distilled in a vacuum. The viscosity of the chlorides falls with increase in their molecular weight. Tri-β-chloroethoxytitanium chloride, both crude and doubly re-distilled, is an extremely viscous (at room temperature) black mass

Thus, the proposed method is sufficiently general, and it is simple to carry out. The transesterification reaction requires very little time and gives an almost quantitative yield.

EXPERIMENTAL

All the experiments described below were carried out with completely dry starting substances and under conditions that prevented the admittance of moisture from the atmosphere.

Preparation of Tri-isoamyloxytitanium Chloride (iso-$C_5H_{11}O)_3$TiCl

A mixture of triethoxytitanium chloride (10 g = 0.046 mole) and isoamyl alcohol (25 g = 0.28 mole) was introduced into a Claisen flask connected to condenser and receiver. The apparatus was protected from the moisture of the air by a drying system. The reaction mixture was heated on an oil bath At a bath temperature of 140-150° a mixture of ethyl and isoamyl alcohols distilled off (b.p. 78-122°, 6.2g). When the temperature of the vapor reached 122°, the reaction mixture was cooled and further isoamyl alcohol (10 g) was added Distillation of the alcohol mixture then proceeded until the boiling point of isoamyl alcohol was reached; this indicated the end of the reaction. The excess of isoamyl alcohol was driven off in a vacuum. The product, which remained in the flask after driving off the alcohol, was distilled over at 174-175° at 2 mm. Yield 13.4 g, corresponding to 85% of theoretical.

On allowing the product to stand, a small number of crystals separated. On the assumption that these crystals consisted of a double compound of tri-isoamyl oxytitanium chloride and isoamyl alcohol, we heated the product in a vacuum (2 hr, 190-210°, 40 mm) in order to break up the double compound. During this time only a few drops of liquid distilled over The product was then distilled twice in vacuo from a Favorsky flask. The tri-isoamyloxytitanium chloride obtained is a colorless viscous hygroscopic liquid, boiling at 173.5-175° at 2 mm: n_D^{20} 1.5092; d_4^{20} 1.0600.

Found %: C 52.21; 52.15; H 9.78; 9.78; Ti 13.98; 14.03

$(C_5H_{11}O)_3TiCl.$ Calculated %: C 52.25; H 9.64; Ti 13.89

Preparation of Tri-β-chloroethoxytitanium Chloride

The reaction between 10 g of triethoxytitanium chloride and 25 g of ethylene chlorhydrin was carried out as in the previous experiment. A mixture of alcohols, boiling from 78 to 90°, was driven off, the bath temperature being 150°. The reaction mixture was cooled, and, after adding 10 g. of ethylene chlorhydrin, distillation was continued, the distillate being almost pure ethylene chlorhydrin. The excess of ethylene chlorhydrin was driven off in a vacuum. The residue distilled at 175-180° at 1.5 mm. Yield 10 g, corresponding to 67% of theoretical. Part of the product polymerized during distillation and remained in the distillation flask as a black powder; this explains the relatively low yield of product. On distilling a second time, the substance boiled at 194-196° at 2 mm. The doubly distilled product, as also the crude material, is a black extremely viscous hygroscopic mass.

Found %: C 22.40; 22.28; H 3.89; 3.84; Ti 14.29; 14.27

$(ClCH_2CH_2O)_3TiCl.$ Calculated %: C 22.39; H 3.76; Ti 14.88

Preparation of Tri-n-butoxytitanium Chloride

The reaction between 8 g of triethoxytitanium chloride and 20 g of n-butyl alcohol was carried out as in the previous experiments. A mixture of alcohols, boiling from 100 to 113° was driven off, the bath temperature being 140°. After cooling the reaction mixture, n-butyl alcohol (12 g) was added, and distillation was continued. Almost pure n-butyl alcohol passed over, and the remainder was removed in a vacuum. The residue distilled at 145-148° at 2 mm. Yield 10 g, corresponding to 90% of theoretical. On distilling a second time, the product boiled at 154-155° at 2 mm. The chloride obtained is a colorless viscous hygroscopic liquid; n_D^{20} 1.5169; d_4^{20} 1.0985.

Found %: C 48.06; 47.98; H 9.03; 9.11; Ti 16.10; 15.84

$(C_4H_9O)_3TiCl.$ Calculated %: C 47.61; H 8.99; Ti 15.82

Preparation of Tri-isobutoxytitanium chloride

Triethoxytitanium chloride (8.8 g) and isobutyl alcohol (25 g) were heated in a Claisen flask with condenser on an oil bath. The receiver contained a small amount of a solution of $AgNO_3$ in absolute alcohol. At a bath temperature of 120°, a mixture of alcohols started to come over. The first 10 ml of distillate contained only traces of chlorine, and then a further 10 ml was distilled over, and this showed a definite reaction for chlorine. The alcohol mixture and the excess isobutyl alcohol were then driven off at 48 mm. The residue distilled at 125-125.5° at 2mm. Yield 9.7 g, corresponding to 90% of the theoretical. On distilling a second time the product all came over at 147-148° at 5 mm. The tri-isobutoxytitanium chloride obtained is a transparent colorless extremely hygroscopic liquid; n_D^{20} 1.5158; d_4^{20} 1.1043.

Found %: C 47.81; 47.68; H 9.08; 9.13; Ti 15.55; 15.69
(C$_4$H$_9$O)$_3$TiCl. Calculated %: C 47.61;   H 8.99;   Ti 15.82

Preparation of Tri-n-hexyloxytitanium Chloride

The reaction between 10.3 g of triethoxytitanium chloride and 25 g of n-hexyl alcohol was carried out as in the previous experiment. At a bath temperature of 150°, practically pure ethyl alcohol distilled over. When 5.1 g of alcohol had distilled over (theoretical 6.4 g), distillation was continued at 44 mm to complete reaction and to remove excess of n-butyl alcohol. Both distillates gave positive reactions for chlorine. If distillation of the alcohols is carried out under more severe conditions, and fresh portions of alcohol are successively added, as usual for transesterification reactions, then appreciable amounts of n-hexyl orthotitanate are formed, and it is difficult to remove these, owing to the closeness of the boiling points of the two reaction products. The residue after removing excess n-hexyl alcohol distilled at 193-196° at 2 mm. Yield 17.7 g, corresponding to 97% of theoretical. On distilling a second time, the product boiled at 182-182.5° at 1 mm. This chloride is a slightly yellowish, comparatively mobile, hygroscopic liquid; n_D^{20} 1.5050; d_4^{20} 1.0039

Found %: C 56.30; 56.31; H 10.28; 10.31; Ti 12.12;
(C$_6$H$_{13}$O)$_3$TiCl. Calculated %: C 55.88;   H 10.16;   Ti 12.38

Preparation of Tri-β-ethoxyethoxytitanium Chloride

The experiment was conducted as indicated for the synthesis of tri-isobutoxytitanium chloride. From a mixture of 10.7 g of triethoxytitanium chloride and 25 g of ethyl cellosolve, 15 ml of alcohol mixture was distilled off. The distillate gave a reaction for chlorine. Further distillation of the mixture of alcohols and the excess of ethyl cellosolve was carried out at 45 mm. The doubly distilled product boiled at 182-183° at 1 mm; n_D^{20} 1.5178; d_4^{20} 1.2035. The yield is almost quantitative.

Found %: C 40.86; 40.91; H 8.11; 8.05; Ti 13.87; 13.71
(C$_2$H$_5$OC$_2$H$_4$O)$_3$TiCl. Calculated %: C 41.09;   H 7.76;   Ti 13.66

SUMMARY

1. A new method is proposed for the synthesis of trialkoxytitanium chlorides by transesterification of the readily accessible triethoxytitanium chloride according to the equation:

$$(C_2H_5O)_3TiCl + 3ROH \rightleftharpoons (RO)_3TiCl + 3C_2H_5OH.$$
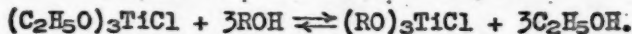
2. The following previously unknown trialkoxytitanium chlorides have been synthesized:

(n - C$_4$H$_9$O)$_3$TiCl,	b.p. 154 - 155°/2 mm
(i-C$_4$H$_9$O)$_3$TiCl,	b.p. 147 - 148°/5 mm
(i-C$_5$H$_{11}$O)$_3$TiCl,	b.p. 173 - 175°/2 mm
(n-C$_6$H$_{13}$O)$_3$TiCl	b.p. 182 - 182.5°/1 mm
(ClCH$_2$CH$_2$O)$_3$TiCl,	b.p. 194 - 196°/2 mm
(C$_2$H$_5$OCH$_2$CH$_2$O)$_3$TiCl	b.p. 182 - 183°/1 mm

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STEREOISOMERIC SODIUM ENOLATES

A. N. Nesmeyanov, B. A. Sazonova, and E. I. Vasilyeva

Like phenylmagnesium bromide [1] and phenyl-lithium [2], phenylsodium in benzene medium combines with benzylideneacetylmesitylene in the 1,4-position, forming a sodium enolate corresponding to the enol form of β,β-diphenylpropionyl-mesitylene.. On benzoylating with benzoyl chloride, an enol-benzoate is formed, m.p. 162°. Comparison of the yields in the 1,4-addition reaction and the benzoylation leads to the conclusion that the whole of the sodium enolate is present in only one configuration, and the same conclusion is reached from the fairly high purity of the crude enol-benzoate obtained and from the impossibility of separating an isomeric O-benzoate from the benzoylation product. It is extremely probable that, as in the case of the 1,4-addition of phenyl-lithium and phenyl-magnesium bromide, the configuration of the sodium enolate obtained in this way (we shall call it enolate I) is in accord with the following equation:

$$C_6H_5CH=CH-C-Mes \qquad C_6H_5 \qquad \overset{H}{\underset{C_6H_5}{CH-C}}=C\overset{Mes}{\underset{OM}{}}$$
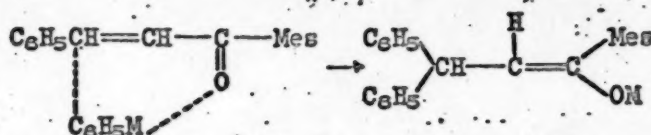
Addition of the molecule C_6H_5M (M is a metal) can be imagined to take place in such a way that the resulting benzhydryl and OM groups are in the cis positions to one another. The methoxymethylation of this enolate gives one of the two possible methoxymethyl O-derivatives, namely the liquid that is obtained from the 1,4-addition product of phenyl-lithium, and at the same time a C-methoxymethyl derivative, m.p. 154-155°, is formed. Thus, simultaneous reaction of the sodium enolate at O and at C is occurring.

The stereoisomeric sodium enolate (enolate II) can be obtained by the enolization of diphenylpropionylmesitylene by means of triphenylmethylsodium. Together with enolate II, a small amount of enolate I is formed. Thus, the enolization of diphenylpropionylmesitylene by triphenylmethylsodium occurs with the formation both of enolate I and of enolate II, the rate of formation of the latter being evidently considerably higher than the rate of formation of enolate I. On benzoylation with benzoyl chloride it gives mainly an enol-benzoate of m.p. 144°. Methoxymethylation leads to an O-derivative of m.p. 92-93°, stereoisomeric with the previous one, and at the same time it gives the same C-methoxy-methyl derivative, m.p. 154°. Here again we have a sodium enolate that reacts in two ways — at O and at C.

Enolate II, although not of very low solubility in benzene (~5%) or ether (~8%) even at room temperature, is much less soluble than enolate I and is therefore relatively readily separated in the solid state. It crystallizes without solvent (benzene). It can be prepared in a pure form by heating enolate I on a boiling water-bath for 1-2 hrs. until as much as possible of the benzene present has been removed and then adding petroleum ether, which leads in the course of a day to the crystallizing-out of enolate II. On benzoylation, pure enolate II gives only the benzoate of m.p. 144°.

Thus, there are two stereoisomeric Na derivatives of diphenylpropionyl-mesitylene, each of which gives only one of the two stereoisomeric benzoates

of the enol form of diphenylpropionylmesitylene. It therefore follows that Enolates I and II are real enolates. With respect to benzoylation and methoxymethylation reactions, they behave like the previously described Li- and MgBr-enolates of diphenylpropionylmesitylene. Nevertheless, there are differences; these concern the considerably greater ease of the interconvertibility of the two sodium enolates. As stated above, Enolate I is converted into Enolate II on heating on a water bath. Under the same conditions Enolate II is partly converted into Enolate I, the reaction evidently tending to an equilibrium with a predominance of Enolate II. For this reason, all the above-described reactions of benzoylation and methoxymethylation were carried out at room temperature, at which no appreciable stereochemical conversion was to be observed; in any case, the rates of formation and of benzoylation of the sodium enolates formed in the two series of experiments are considerably greater than the rates of the cis-trans conversions.

It may be considered that the Na enolate dissociates on heating into ions:

$$\underset{C_6H_5}{\overset{C_6H_5}{}}CH-CH=C\underset{O'}{\overset{Mes}{}} \quad \text{and Na}^+$$
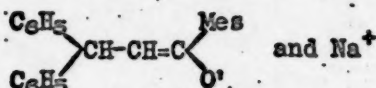
and that the stereoisomerization of the enolate proceeds through the ionization stage.

It is interesting to note that in presence of metallic sodium the rate of the conversion of Enolate I into Enolate II is reduced. Whether the cause for this is the opposed conversion of Enolate II into Enolate I under the action of the alkali metal (which is generally characteristic for cis-trans isomers), to which reference has been made previously, at present remains unexplained, in as much as Enolate II, on heating, is partly converted into Enolate I. Thus, the sodium enolates are considerably more labile than the lithium and particularly the magnesium enolates, which, of course, is not at all unexpected, though it makes it considerably more difficult to obtain reliable results.

Nevertheless, the fact of obtaining a definite enol-benzoate (or O-methoxymethyl derivative) by the benzoylation (or methoxymethylation) at room temperature of a definite stereoisomer of the enolate shows without doubt that these reactions proceed with non-ionized sodium enolates, for there would otherwise be obtained, in each case, either the same mixture of stereoisomers or just one stereoisomer – the more stable. The quaternary ammonium enolates behave in this way, which is shown in the previous and in the present work.

Thus, also in the case of sodium enolates must the hypothesis that explains the dual (at C and at O) reactivity by the reaction of a mesomeric anion be considered to be invalid. Also invalid, of course, is the suggestion that tautomeric conversion (reversible isomerization):

$$-\overset{H}{C}=\overset{}{\underset{ONa}{C}}- \quad \underset{(1)}{\rightleftarrows} \quad -\overset{H}{\underset{Na}{C}}-\overset{}{\underset{O}{C}}- \quad \underset{(2)}{\rightleftarrows} \quad -\overset{}{C}=\overset{}{\underset{H\ ONa}{C}}- ,$$
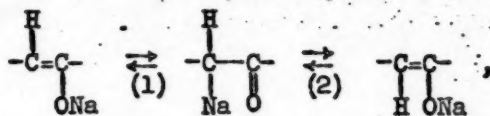
is the cause of the dual reactivity of sodium enolates. If this were true under the conditions of the reactions studied, then equilibrium would be established in accordance with these equations (1 and 2), and benzoylation (and methoxymethylation) would lead to the same mixture of products whether Enolate I or Enolate II were employed. It is clear that the reagent did not act on a system in which an equilibrium had been established. In just the same way, it cannot be supposed that appreciable conversion of enolate into the keto form could occur in the reactions studied (C-methoxymethylation), to say nothing of the attaining of an equilibrium, and at the same time no conversion of the keto form into the stereoisomeric enolate (presence in the benzoylation or methoxymethyl-

ation products of only one stereoisomer of the enol derivative). If, indeed, for one moment we assume the formation of the keto form, then evidently, under the conditions of the equilibrium that would be assumed in this case, the enol forms would predominate, and the rate of keto-enol conversion would be greater than that of the reverse reaction. Thus, if the keto form were formed, the second enol form would be produced in great quantity and, under the conditions of the experiment, would be found in the form of esters or ethers. This conclusion is in accord with the result of C-alkylation of acetoacetic ester in aqueous alkaline medium [3].

Again, experiment rejects the supposition, which is improbable in itself and is contradictory to the usual concepts, that first of all a sodium ion dissociates, and then a slow isomerization (electrono-isomerization) of the anion occurs (more slowly than the reaction with benzoyl chloride):

$$
\begin{array}{c}
C_6H_5 \\
C_6H_5
\end{array}
CH-CH=C
\begin{array}{c}
Mes \\
ONa
\end{array}
\rightarrow
\begin{array}{c}
C_6H_5 \\
C_6H_5
\end{array}
CH-CH=C
\begin{array}{c}
Mes \\
O^9
\end{array}
+ Na^+ \rightarrow
$$

$$
\rightarrow
\begin{array}{c}
C_6H_5 \\
C_6H_5
\end{array}
CH-C'H-\overset{\displaystyle O}{\underset{\displaystyle \|}{C}}-Mes
$$

and finally reaction occurs at the C atom. If under the conditions of the reaction of a ketone-anion of this sort were formed, then there would be no reason why electrono-isomerization at at least the same rate should not occur into the stereoisomeric enolate anion, the presence of which would be revealed by the benzoylation or methoxymethylation.

Thus, replacement of the Na cation by the $C_6H_5(CH_3)_3N$ cation (which is known to be incapable of being covalently bound and is certain, therefore, to form an ionic system) in Na enolates I and II and subsequent benzoylation leads in both cases to a mixture of stereoisomeric enol-benzoates. If the enolate (after replacing the Na cation by $C_6H_5(CH_3)_3N^+$) is methoxymethylated, then again a mixture of stereoisomeric O-derivatives is formed; at the same time, the ammonium enolate, in contrast with the Na enolate, does not give a C-derivative. The alkylation and acylation of the ammonium enolates of carbonyl compounds will be the subject of a future investigation.

Thus, the most natural concept concerning the cause of the dual reactivity (at O and at C) of metal enolates still remains, in our opinion, after considering the results of experiments with sodium enolates, the concept that we have brought forward concerning the transfer of the reactive center of the molecule along the system of conjugated (Na—O)- and (C=C)-bonds:

$$
\begin{array}{c}
H_5C_6 \\
H_5C_6
\end{array}
CH-CH=C
\begin{array}{c}
Mes \\
O \\
Na
\end{array}
$$

When an electrophilic reagent attacks at C, the electron pair of the future covalent bond is called away from the oxygen to the carbon, as shown by the arrows. In our opinion, the picture as a whole becomes quite convincing on comparing our results on magnesium, lithium, sodium and ammonium enolates.

At first glance, the unexpected orientation (from the point of view of our hypothesis) of the methoxymethylation of an ammonium enolate (as distinct

from MgBr, Li, and Na enolates) only on to O merits attention. An interesting parallel is the O-acetylation of acetoacetic ester in pyridine. Discussion of this question would be premature, for there are too few data, but we hope to turn to it later.

In connection with our present series of experiments, the natural question arises concerning the character of the dual (keto and enol) reactivities of keto and enol compounds. We suppose that in a large number of cases in which keto compounds react in enol-fashion (and enols in keto-fashion) the reaction proceeds with transfer of the reactive center without preliminary tautomeric change. This concerns, above all, cases of so-called pseudomerism.

EXPERIMENTAL

I. Addition of Phenylsodium to Benzylideneacetylmesitylene

Benzylideneacetylmesitylene (3 g) in absolute benzene (10 ml) is added to phenylsodium, obtained from 1 g (0.0043 g-atom) of sodium and 2.25 (0.02 mole) of chlorobenzene.

After being heated for 30 min. at 30-40°, the enolate solution is filtered from excess sodium and NaCl and titrated. The benzene solution (23 ml; 0.0077 g Na in 1 ml) is decomposed and washed with water; the benzene is driven off, and absolute alcohol is added to the residue.

Yield of β,β-diphenylpropionylmesitylene: 1.9 g (75% of theoretical); m.p. 78-79°. After two crystallizations from alcohol: m.p. 80-81°. Mixed test with known diphenylpropionylmesitylene melts without depression.

II. Benzoylation of the Na Enolate[1] Produced by the 1,4-Addition of Phenylsodium to Benzylideneacetylmesitylene

Benzoyl chloride (0.94 g) in absolute benzene (2 ml) is added to 22 ml of a solution of Na enolate I (0.0070 g Na per ml). The reaction mixture is decomposed by water, the benzene layer is washed with water, the benzene is driven off, and acetone is added to the residue. The crystals that separate are filtered off and washed with acetone. Yield of enol-benzoate: 2.37 g (80% of theor.); m.p. 156-157° (before recryst.). After recrystallization from acetone: m.p. 161-162°. Mixed test with benzoate of m.p. 162° (prepared by the benzoylation of the MgBr enolate) melts without depression.

III. Heating (80°) of Na Enolate I

1. Without metallic sodium. A benzene solution of Na enolate I (24 ml; 0.0071 g Na per ml) was boiled for 1.5 hr and then benzoylated. The reaction mixture was decomposed with water, the benzene was evaporated off, and acetone was added to the residue. The enol-benzoate isolate (0.9 g: 28% of theor.) melts at 158-160° (not recryst). From the acetone solution a mixture of enol-benzoates (1.42 g: 44% of theor.; m.p. 122-123°) was obtained; from this an enol-benzoate of m.p. 140-141° (0.27 g: 8% of theor.) was separated; m.p. after recrystallizing twice from acetone — 144°.

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[1] This Na enolate will be called in future Na enolate I, and the isomeric enolate, Na enolate II.

2. In presence of metallic sodium. Metallic sodium (0.15 g) was added to 22 ml of a benzene solution of Na enolate I, and the mixture was heated at 80 deg for 1.5 hr. After benzoylation and suitable treatment, as described in the previous experiment, an enol-benzoate (1.45 g, 49% of theor.) of m.p. 156-158° (after recrystallization 159-160°) and a mixture of benzoates (0.7 g: 24% of theor.) were obtained by fractional crystallization of the mixture an enol-benzoate (0.15 g: 5% of theor.) of m.p. 140-141° (144° after double recrystallization) was separated.

IV. Methoxymethylation of Na Enolate I

Chloromethyl methyl ether (2.4 g: 100% excess) in absolute benzene (2 ml) is added to 35 ml of a benzene solution of enolate I (0.0095 g Na per ml). The reaction mixture is decomposed with an aqueous solution of caustic soda, the benzene layer is washed with water, the benzene is evaporated off. The precipitated crystals are filtered from the oil and washed with petroleum ether. Yield of C-methoxymethyl derivative: 2.26 g (42% of theor.); m.p. 151-152°. M.p. after recrystallization from methyl alcohol: 154-155°. Mixed test with known sample showed no depression of m.p. Data in literature: m.p. 155° (Kohler [5]; Nesmeyanov and Sazonova [2]).

After evaporating off the petroleum ether, the oil was distilled in a vacuum: b.p. 215-217°, 2.5 mm. Yield of the O-methoxymethyl derivative of diphenylpropionylmesitylene 1.84 g (34% of theor.). On introducing nuclei of solid O-derivative, crystallization did not set in. Data in literature: b.p. 216-218°, 3 mm [2].

V. Hydrolysis of the Liquid O-Methoxymethyl Derivative

The liquid O-methoxymethyl derivative of diphenylpropionylmesitylene (0.59 g) was boiled with 10 ml conc. HCl for 1 hr. (after boiling for a few minutes the aqueous solution gives a reaction with fuchsin-sulfurous acid). The mixture was diluted with water, the oil extracted with ether, and the ether driven off. M.p. after recrystallization from alcohol: 80°. Yield of β,β-diphenylpropionylmesitylene: quantitative. After repeated recrystallization, m.p. 81-82°. Mixed m.p. with known sample showed no depression.

VI. Reaction of Na Enolate I with Trimethylphenylammonium Benzenesulfonate

1. Benzoylation. A benzene solution of Na enolate I (29 ml; 0.0070 g Na per ml) is divided into two parts. To one is added trimethylphenylammonium benzenesulfonate (2.7 g: 100% excess). Each portion is stirred at room temperature for one hour and then benzoylated.

a) From the portion without ammonium salt (14 ml of enolate solution) the following were separated after benzoylation: 1.47 g (79% of theor.) of enolbenzoate, which after recrystallization from acetone has m.p. 161-162° (not recryst: 155-156°), and 0.02 g of a mixture of enol-benzoates, m.p. 123-127°.

b) The portion with ammonium salt (15 ml of enolate solution) was treated in the following way. The precipitate was filtered off, carefully washed with benzene, dried in a stream of dry nitrogen, and analyzed for Na:

Found %: Na 0.94; 0.88.

This points to the presence in the precipitate of sodium benzenesulfonate formed as a result of double decomposition of the salts.

The filtrate was benzoylated and there were obtained as products: 0.33 g (16% of theor.) enol-benzoate of m.p. 154-155°, melting, after recrystallization from acetone, at 161°, and 0.72 g (37% of theor.) of a mixture of enol-benzoates of m.p. 122-125°, from which, by fractional crystallization, an enol-benzoate of m.p. 140-141° (0.14 g: 7% of theor.) was separated. After recrystallization from acetone the m.p. of the substance obtained and the mixed m.p. of a mixed test with a known sample was 143-144°. On hydrolyzing the mixture of enol-benzoates (m.p. 122-125°), β,β-diphenylpropionylmesitylene was obtained in 97% yield[1]).

2. Methoxymethylation. Trimethylphenylammonium benzenesulfonate (9g: 25% excess) is added to 46 ml of a benzene solution of Na enolate I (0.017 g-atom Na per ml). The reaction mixture is stirred for 2.5 hr at room temperature, then chloromethyl methyl ether (13.6 g: 100% excess) in 20 ml of absolute benzene is added, and the mixture is allowed to stand for 1 hr. After decomposition with aqueous alkali, washing the benzene layer with water, and evaporation of the benzene, no C-derivative was obtained. A solid O-derivative (2.0 g) of m.p. 81° was separated from the oil. After the O-derivative had been recrystallized from alcohol, it melted at 90°, both alone and when in admixture with a known sample. Yield 1.8 g (20% of theor.).

The oil that had not crystallized was vacuum-distilled: b.p. 218-220°/3 mm Yield of liquid O-derivative, stereoisomeric with the previous one: 5.05 g (56% of theor.).

VII. Enolization of β,β-Diphenylpropionylmesitylene by Phenylsodium, and Subsequent Benzoylation

1) β,β-Diphenylpropionylmesitylene (2 g) in 10 ml of absolute benzene is added to phenylsodium prepared from 0.7 g (0.03 g-atom) of sodium and 1.37 g (0.012 mole) of chlorobenzene. The reaction mixture is warmed for 30 min., after which time an addition is made of 2.14 g of benzoyl chloride. The mixture is decomposed with water, the benzene layer is washed, the benzene is driven off, and acetone is added to the residue. The crystals are filtered off and washed with acetone. A mixture of the cis and trans isomeric enol-benzoates, m.p. 123-126°, is obtained. Yield 1.95 g (75% of theor.). M.p. unchanged by recrystallization.

Found %: C 86.08, 86.04; H 6.75, 6.67.
$C_{31}H_{28}O_2$. Calculated %: C 86.07; H 6.52.

A benzoate of m.p. 160-161° (0:2 g) and a benzoate of m.p. 143-144° (0.2 g were isolated from the mixture obtained.

2) Hydrolysis of the mixture of benzoates: the mixture of benzoates of m.p. 123-126° (1 g) was boiled for 30 min. with an alcoholic solution containing 0.2 g of caustic soda, and the mixture was then diluted with water, the oil was extracted with benzene, the benzene solution was washed with water, and the benzene was evaporated off. Absolute alcohol was added to the residue and the crystals that separated were filtered off; m.p. 80-81°. Yield of β,β-diphenylpropionylmesitylene 0.74 g (98% of theor.).

VIII. Enolization of β,β-Diphenylpropionylmesitylene by Metallic Sodium, and Subsequent Benzoylation

Diphenylpropionylmesitylene (1 g) in 10 ml of absolute toluene was boiled with 0.15 g of metallic sodium for 2 hr, and benzoyl chloride (0.35 g) was then added (solution first poured off metallic sodium).

___

[1]) The benzoate of m.p. 162° is not converted into a mixture of cis and trans isomeric enol benzoates under the action of trimethylphenylammonium benzenesulfonate

The reaction mixture was decomposed with water, the toluene layer was washed with water, and the toluene was evaporated off. The crystals that separated after adding acetone were filtered off and washed with acetone. The products obtained were 0.22 g (17% of theor.) of an enol-benzoate of m.p. 154-156°, recryst. m.p. 160-161°, and 0.26 g of a mixture of enol-benzoates, m.p. 124-126°, from which, by fractional crystallization, an enol-benzoate of m.p. 140-141° (0.07 g; 5% of theor.) was separated – m.p. after two recrystallizations 144°. The total yield of enol-benzoates was 37% of theoretical.

IX. Conversion of α-Bromo-β,β-diphenylpropionylmesitylene into Enolate I by the Action of Phenylsodium, and Subsequent Benzoylation[1])

α-Bromo-β,β-diphenylpropionylmesitylene (3 g) in 30 ml of absolute benzene is added to phenylsodium prepared from 0.85 g (0.037 g-atom) of sodium and 1.67 g (0.015 mole) of chlorobenzene. After heating for 1 hr at 40-50°, benzoyl chloride (2.6 g) is added, and the mixture is heated for a further half hour. The separation of the benzoate is described above; m.p. 155-157° (not recryst.). Yield 1.35 g (42% of theor.). After recrystallizing twice from acetone, m.p. 162°.

X. Enolization of β,β-Diphenylpropionylmesitylene by means of Triphenylmethylsodium

1) Benzoylation. β,β-Diphenylpropionylmesitylene (1.2 g) is added to 45 ml of an ethereal solution of triphenylmethylsodium containing 0.022 g of $(C_6H_5)_3CNa$ per ml; then benzoyl chloride (0.51 g) is added. The mixture is decomposed with water, the ethereal solution is washed, and the ether is evaporated off. The crystals that separate after adding acetone are filtered off and washed with acetone. An enol-benzoate (0.95 g: 60% of theor.) of m.p. 134-136° is obtained. After recrystallizing from acetone it melts at 143-144°, both alone and in admixture with known material. After removing triphenylmethane from the mother liquor, a mixture of enol-benzoates (0.25 g) of m.p. 124-125° was separated.

2) Methoxymethylation of Na enolate II. β,β-Diphenylpropionylmesitylene (2.25 g) is added to 54 ml of an ethereal solution of triphenylmethylsodium (0.035 g per ml); chloromethyl methyl ether (1.2 g: 100% excess) is then added. The mixture is decomposed with an aqueous solution of caustic soda, the ethereal layer is washed with water, the ether is distilled off, and petroleum ether is added to the residue. The crystals that separate are filtered off and recrystallized from methanol. The C-methoxymethyl derivative, m.p. 153-154°, is obtained. Yield 1.2 g (47% of theor.): a mixed test with known C-derivative gave no depression of m.p. After evaporating off the petroleum ether, the residue was recrystallized from benzene, m.p. 91-92°. Mixed test with triphenylmethane melted at 91-92°.

The O-methoxymethyl derivative of diphenylpropionylmesitylene (0.2 g: 8% of theor.) was separated from the filtrate after removal of benzene. The m.p. after recrystallization from methanol was 92-93°. A mixed test with known O-derivative showed no depression of m.p. A mixed test with triphenylmethane gave m.p. 67-70°. Data from literature: m.p. 92° [5], 92-93° [2].

XI. Hydrolysis of the Solid O-Methoxymethyl Derivative

This substance (0.30 g) was boiled with 8 ml of conc. HCl for 1 hr (the aqueous solution gives, after a few minutes' boiling, a reaction with fuchsin-sulfurous acid). The reaction mixture was diluted with water, the oil was extracted with ether, the ether was evaporated off, and the residue was recrystal-

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[1]) In the case of the magnesium derivative of diphenylpropionylmesitylene, this method yields MgBr enolate II [4].

lized from absolute alcohol, m.p. 81-82°. Yield of diphenylpropionylmesitylene 0.25 g (96% of theor.).

XII.   Isolation of Na Enolate II.   Its Properties.

The benzene solution of Na enolate I, obtained by adding phenylsodium to ben-zylideneacetylmesitylene, is filtered from Na and NaCl. The benzene is driven off and the residue is heated for 2 hr on a boiling water-bath (Na enolate I is con-verted by heat into Na enolate II); petroleum ether is then added, and the solution is left for 24 hr for the crystallization of Na enolate II to occur. The precipi-tated crystals are filtered off, washed 4 times with petroleum ether, and dried by the prolonged passage of a stream of pure dry nitrogen.

Na enolate II is in the form of crystals of a slightly yellow color. It is fairly soluble in ether (8 g in 100 ml of ether at 20°), rather less in benzene (5 g in 100 ml of benzene at 20°).

$$\text{Found \%: Na } 6.68; \ 6.55$$
$$C_{24}H_{23}ONa. \quad \text{Calculated: Na } 6.56$$

1) Na enolate II (0.39 g) was decomposed with water, the oil was extracted with benzene, and the benzene was evaporated off. Absolute alcohol was added to the residue. Yield of β,β-diphenylpropionylmesitylene 0.34 g (95% of theor.); m.p. 79-80°. After two recrystallizations from alcohol m.p. 81-82°.

2) Benzoylation. Enolate II (0.846 g) and absolute benzene (5 ml) were mixed for 1 hr at room temperature (for better dissolution), and then benzoyl chloride (0.34 g) was added. After the usual treatment the enol-benzoate (0.719 g: 6% of theory) of m.p. 140-141° was separated. After recrystallizing twice from acetone, it melted at 144-145°.

3) Conversion of Na enolate II into Na enolate I. Na enolate II (0.282 g) in 5 ml benzene was boiled for 1.5 hr and then benzoylated. A mixture of enol-benzoates (0.230 g: 72% of theor.) was obtained, and from these an enol-benzoate (0.03 g: 9% of theor.) of m.p. 159-160° (recryst. 160-161°)was separated.

XIII.   Reaction of Na Enolate II with Trimethylphenylammonium Benzenesulfonate

Na enolate II (1.364 g) and trimethylphenylammonium benzenesulfonate (2.3 g: 100% excess) were stirred in benzene for 1 hr at room temperature. After benzoylation, a mixture of enol-benzoates (1.037 g: 62% of theor.) was ob-tained, and from this an enol-benzoate (0.28 g: 16% of theor.) of m.p. 157-158° (double recryst. 160-161°) and an enol-benzoate (0.12 g: 7% of theor.) of m.p. 140-141° were isolated; the latter, after recrystallizing twice from acetone gave a m.p. and a mixed m.p. of 144-145°.[1]

SUMMARY

1. It has been shown, on the basis of β,β-diphenylpropionylmesitylene as example, that the sodium derivatives of keto compounds exist in two cis - trans stereoisomeric forms, and that they are therefore enolates.

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[1] 1-Benzoylation of Na enolate II (blank experiment), see Expt. XII, 2; 2- the benzoate of m.p. 144° when submitted to the action of triphenylmethylammonium benzenesulfonate is not converted under the same conditions into a mixture of cis and trans isomeric enol-benzoates.

2. On benzoylating the stereoisomeric Na enolates at room temperature, the corresponding stereoisomeric enol-benzoates are formed. On methoxymethylating, they give the corresponding stereoisomeric O-methoxymethyl derivatives together with one form only of C-methoxymethyl derivative.

3. On replacing Na by $(CH_3)_3C_6H_5N^+$, the stereoisomers, instead of reacting differently, react in identical fashion (with benzoyl chloride and chloromethyl methyl ether). Also, a C-methoxymethyl derivative is not formed.

4. It has been shown that the sodium enolates are considerably more labile than the lithium and, particularly, the magnesium enolates, which were studied previously. Thus, on heating, the sodium enolates are mutually converted, giving a mixture in which the more stable enolate predominates.

5. As in the case of the Li and MgBr enolates, the conclusion is reached that the dual reactivity (alkylation or acylation on O and on C) of Na enolates is, in the first place, not due to the reversible isomerization (tautomerization) of these enolates into a keto form containing a C-metal bond and, in the second place, not due to the presence of an ionic structure in these enolates and to dual reactivity in the mesomeric ion.

6. The hypothesis previously put forward concerning the transfer of the reactive center of the molecule along a system of conjugated (Na — O and C=C) bonds as the cause of the dual reactivity (at O and at C) of metal enolates is confirmed.

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SYNTHESIS OF ISOXAZOLES FROM β-CHLOROVINYL KETONES

N.K.Kochetkov, A.N.Nesmeyanov, and N.A.Semenov.

As we have recently shown [1], methyl β-chlorovinyl ketone is a convenient starting material for the synthesis of various heterocyclic compounds, including methylisoxazole. On the basis of this reaction we have developed a new general method for the synthesis of alkylisoxazoles, which have until now been practically unstudied owing to their inaccessibility.

The reaction of alkyl β-chlorovinyl ketones, which are readily prepared by the method described by us in conjunction with Rybinskaya [2], with hydroxylamine hydrochloride is most conveniently carried out in methanol, although other solvents, such as acetic acid, may be used. The lower alkylisoxazoles (methyl- and ethyl-) are appreciably volatile in alcohol vapor and are soluble in water, and therefore in separating them from the reaction mixture we made use of the ability of isoxazoles to give crystalline complexes with cadmium chloride [3]; using these complexes, we separated them in much the same way as we have described for methylisoxazole [1]. On the other hand, the higher homologs are of low solubility in water, and their separation can be carried out without difficulty by the usual method. We have prepared by the method described methyl-, ethyl-, propyl-, and isobutylisoxazoles with yields of 60-70%.

On treating our methylisoxazole with sodium ethoxide in ether, following Claisen [4], cyanoacetone was separated in the form of its sodium salt; it was identified by conversion into the phenylhydrazone. This proves the presence of α-methylisoxazole in the substance that we obtained. From the reaction mixture, after removing the sodium salt of cyanoacetone, we isolated pure γ-methylisoxazole. Using the procedure developed by Claisen [4], we determined the content of α-isomer in the alkylisoxazoles that we obtained (from the weight of the salt of the corresponding cyanoketone that was separated); it varied from 60 to 68%. Thus, it was shown that the alkylisoxazoles that we obtained were mixtures of γ- and α-isomers:

$$R-\overset{\displaystyle C}{\underset{N}{|}}\overset{\displaystyle CH}{\underset{CH}{|}} \longleftarrow RCOCH=CHCl \longrightarrow \overset{CH-CH}{\underset{N\ \ C-R}{|\quad|}}$$
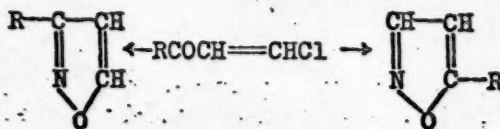
The question of the mechanism of the simultaneous formation of the two isomers was not specially investigated by us. It is most probable that the formation of a mixture of isomers is brought about by two competing reactions:

97

$$\left[\begin{array}{c} \text{RC—CH=CHCl} \\ \overset{|}{\text{NOH}} \end{array}\right] \longleftarrow \text{RCOCH}\!=\!\text{CHCl} \longrightarrow \left[\text{RC—CH}\!=\!\text{CH—NHOH}\right]$$
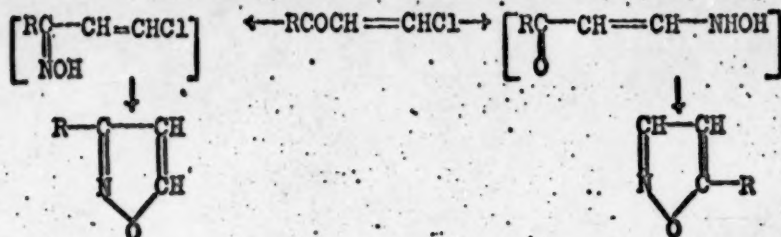
However, another possibility is not altogether excluded, namely that alkyl β-chlorovinyl ketone at first goes over into some sort of intermediate compound, which then gives α- and γ-isomers simultaneously. The intermediate compound could be either the so-called "sesquioxime", which has been shown [5] to be formed intermediately in the synthesis of isoxazoles from hydroxymethylene ketones, or the acetal of a β-ketoaldehyde, which, as shown by us and Rybinskaya [6], is readily formed by the action of alcohol on a β-chlorovinyl ketone; in our case, alcohol was used as solvent.

By using the method we have developed for the synthesis of isoxazoles, we were able to obtain, apart from alkylisoxazoles, previously inaccessible isoxazoles containing halogen in the side-chain. For this purpose we used the reaction of chloromethyl β-chlorovinyl ketone with hydroxylamine, and obtained as a result chloromethylisoxazole. The procedure for the synthesis of chloromethyl β-chlorovinyl ketone from chloroacetyl chloride, given by English authors [7], was improved by us, and the yield of chloromethyl β-chlorovinyl ketone was raised to 80%. This compound by reaction with hydroxylamine under the usual conditions gives chloromethylisoxazole with a yield of 85%. It was found, unexpectedly, that the substance obtained was not split with sodium alkoxide, which points to the absence therein of α-isomer and gives us the right to regard it as pure γ-chloromethylisoxazole. This compound is very interesting in connection with the synthesis of completely inaccessible isoxazole derivatives, which have recently assumed practical importance as physiologically active substances. As was to be expected, the Cl atom in γ-chloromethylisoxazole is very readily replaced by nucleophilic groups. Thus, reaction with NaBr and NaI leads to bromo- and iodo-methylisoxazole, and reaction with NaCN in alcohol gives 3-isoxazole-acetonitrile, which can act as starting material for further interesting syntheses;

$$\text{ClCH}_2\text{C—CH} \xrightarrow{\text{MeX}} \text{XCH}_2\text{C—CH}$$
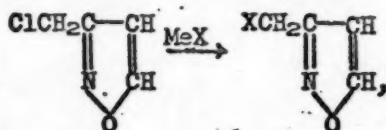
where X = Br, I, or CN.

All the newly prepared representatives of the isoxazole class are mobile liquids of characteristic odor. Alkylisoxazoles very slowly darken on storing. In the calculation of the molecular refractions of the compounds prepared we used Auwers' data [8], but in all cases obtained low values in comparison with the calculated values. This shows that the increment recommended by Auwers for nitrogen in the isoxazole ring (3.901) is not satisfactory and requires revision. In fact, the mean departure for the isoxazoles prepared by us and also for the previously known representatives of this series, which were used by Auwers for his calculations, is 1.19. Auwers assumes for the nitrogen increment of isoxazoles the value for aliphatic oximes, and the departure of the values found from the calculated values he regards as "negative exaltation". Such a point of view is hardly valid.

The cyclic system of isoxazole has a number of peculiarities that bring it close to aromatic compounds, which may be illustrated, for example, by the ease of electrophilic substitution reactions. It is quite natural, therefore, that an atom of nitrogen, when contained in the isoxazole system, should acquire a quite different character, sharply differentiated from the character of a nitrogen atom in an aliphatic oxime. The calculations we have made show that more satisfactory agreement is obtained between the values for the molecular refractions of isoxazoles when the value of the nitrogen increment is assumed to be that of the nitrogen of a tertiary amine (2.84).

EXPERIMENTAL

I. Chloromethyl β-Chlorovinyl Ketone

Aluminum chloride (180.0 g) is added gradually over 1 hour with energetic stirring to 113.0 g of chloroacetyl chloride, and acetylene is passed in a rapid stream for 6 hours; the temperature of the reaction mass is maintained at 25-35°. The reaction mass is poured on to ice and extracted with ether; the extract is dried over calcium chloride; the solvent is driven off, and the residue is vacuum-distilled, the fraction boiling at 62-65° at 8-10 mm being collected. Yield 87.7 g (84% of theoretical, calculated on aluminum chloride, 65% of theoretical, calculated on chloroacetyl chloride). The pure substance has b.p. 58-59°/7 mm; 73-75°/15 mm. (Data in literature: [7]): 71-74°/10 mm; [9] 71-72.5°/12 mm).

II. Methylisoxazole

Methyl β-chlorovinyl ketone (24.0 g) is added to a solution of 15.0 g of hydroxylamine hydrochloride in 200 ml of methanol, and the mixture is heated for 3 hours on a water-bath. A saturated aqueous solution of cadmium chloride (80 g) is then added to the hot mixture, and the mixture is then again heated to boiling and left to stand overnight. The precipitate of the complex is filtered off, washed with a solution of cadmium chloride, transferred wet to a Wurtz flask, and there decomposed by heat. The distillate is saturated with sodium sulfate, the oily layer of methylisoxazole is separated, and the aqueous layer is extracted with ether. The extract, united with the main portion of the substance, is dried over magnesium sulfate, the ether is driven off, and the residue is distilled from a Favorsky flask with a good fractionating column. Yield 11.2 g (58.4% of theoretical). After a second distillation the substance has the following constants: b.p. 118-122°; d_4^{20} 1.0283; n_D^{20} 1.4380; found MR_D 21.21; for C_4H_5ON calculated MR_D (according to Auwers) 22.45; calculated MR_D (nitrogen increment 2.84) 21.39. (Data in literature [8]: α-methylisoxazole, b.p. 122°; d_4^{20} 1.023; n_D^{20} 1.439; γ-methylisoxazole, b.p. 118°; d_4^{20} 1.022; n_D^{20} 1.435).

Found %: C 57.84; 57.76; H 6.20; 6.10; N 17.00; 16.95;
C_4H_5ON. Calculated %: C 57.85; H 6.03; N 16.86.

Methylisoxazole is a colorless mobile oil with an odor reminiscent of that of pyridine. It is fairly soluble in water. It may be preserved for a long period without change.

III. Treatment of Methylisoxazole with Sodium Ethoxide

Methylisoxazole (10.0 g) is treated in the cold with a solution of sodium ethoxide prepared by dissolving 2.5 g of sodium in 50 ml of alcohol; absolute ether (40 ml) is then added. After 1 hour the precipitated sodium salt of cyanoacetone is filtered off; the filtrate is neutralized with hydrochloric acid to phenolphthalein and extracted with ether. The ether is driven off, and a saturated aqueous solution of cadmium chloride is added to the residue. After 2

hours, the precipitate of the complex is filtered off and decomposed by heat, while still in the wet condition, in a Wurtz flask. The distillate is extracted with ether, the extract is dried over magnesium sulfate, and the ether is driven off. On distilling the residue, γ-methylisoxazole (2.3 g) was obtained; it gave no precipitate on treatment with sodium ethoxide. The substance has b.p. 118°; d_4^{20} 1.0206; n_D^{20} 1.4348. (Data in literature: [8]): b.p. 118°; d_4^{20} 1.022; n_D^{20} 1.435.)

A small amount of the sodium salt of cyanoacetone was dissolved in aqueous acetic acid and phenylhydrazine was added; the precipitate formed was filtered off and, after recrystallization from alcohol, was obtained as colorless crystals m.p. 100° (data in the literature for the phenylhydrazone of cyanoacetone: [5] m.p. 101-102°; [10] m.p. 96-97°).

The same experiment was carried out quantitatively: from 4.620 g of methylisoxazole 4.008 g of the sodium salt of cyanoacetone was obtained, corresponding to a content in the mixture of 68% α-isomer.

IV. Ethylisoxazole

This was prepared and isolated analogously to methylisoxazole (Section II) from 5.6 g of hydroxylamine hydrochloride and 9.2 g of ethyl β-chlorovinyl ketone in 70 ml of methanol. Yield 4.55 g (60% of theoretical). After redistilling, the ethylisoxazole had the following constants: b.p. 139-140°; d_4^{20} 0.9916; n_D^{20} 1.4440; found $\underline{MR}_D$ 26.02; for C_5H_7CN calculated $\underline{MR}_D$ (according to Auwers) 27.07; calculated $\underline{MR}_D$ (nitrogen increment 2.84) 26.01.

<div align="center">

Found %: N 14.43; 14.30
C_5H_7ON. Calculated %: N 14.41.

</div>

Ethylisoxazole is a colorless oil with an odor reminiscent of pyridine. It may be preserved a long time without change. After treating 0.931 g of the substance as described under Section III, 0.682 g of precipitate was obtained, corresponding to an α-isomer content of 59.7%.

V. Propylisoxazole

Propyl β-chlorovinyl ketone (9.6 g) was added to a solution of 6.0 g of hydroxylamine hydrochloride in 70 ml of methanol, and the mixture was heated on the water-bath for 3 hours. To this, on cooling, four times its volume of water was added, and the oil that separated was extracted several times with ether. The extract was dried over magnesium sulfate, the ether was driven off, and the residue was vacuum-distilled. Yield 5.8 g (73% of theoretical). After repeated distillation, the substance had the following constants: b.p. 160-161°; 69-70°, 35 mm; d_4^{20} 0.9722; n_D^{20} 1.4468; found $\underline{MR}_D$ 30.26; for C_6H_9ON calculated $\underline{MR}_D$ (according to Auwers) 31.69; calculated $\underline{MR}_D$ (nitrogen increment 2.84) 30.63.

<div align="center">

Found %: 12.39; 12.35
C_6H_9ON. Calculated %: N 12.60

</div>

Propylisoxazole is a colorless oil with a characteristic odor; it is insoluble in water. It slowly darkens on keeping. After treating 2.059 g of the substance with sodium ethoxide, as indicated in Section III, 1.656 g of precipitate is obtained, corresponding to an α-isomer content of 67.2%.

VI. Isobutylisoxazole

This was prepared and isolated as indicated in Section V from 5.0 g of hydroxylamine hydrochloride and 10.0 g of isobutyl β-chlorovinyl ketone in 100 ml. of

methanol. Yield 6.0 g (70% of theoretical). After redistilling, the isobutylisoxazole had the following constants: b.p. 168-169°; d_4^{20} 0.9450; n_D^{20} 1.4480; found. MR_D 35.46; for $C_7H_{11}ON$ calculated MR_D (according to Auwers) 36.31; calculated MR_D (nitrogen increment 2.84) 35.25.

Found %: N 11.46, 11.54
$C_7H_{11}ON$. Calculated %: N 11.19

Isobutylisoxazole is a colorless oil with a characteristic odor. It is insoluble in water. It slowly darkens on keeping.

VII. 3-Chloromethylisoxazole

This was prepared and isolated as indicated in Section V from 11.0 g of hydroxylamine hydrochloride and 19.4 g of chloromethyl β-chlorovinyl ketone in 100 ml of methanol. Yield 13.8 g (85% of theoretical). After redistilling, the substance had the following constants: b.p. 65-66° at 20 mm; 49-50° at 7 mm; d_4^{20} 1.2745; n_D^{20} 1.4810; found MR_D 26.28; C_4H_4ONCl: calculated MR_D (according to Auwers) 27.32; calculated MR_D (nitrogen increment 2.84) 26.26.

Found %: N 11.72
C_4H_4ONCl. Calculated %: N 11.91

Chloromethylisoxazole is a colorless oil, insoluble in water. It possesses lachrymatory properties. On treating the substance with sodium ethoxide, a precipitate was obtained only after 24 hours, and this consisted entirely of sodium chloride.

VIII. 3-Bromomethylisoxazole

3-Chloromethylisoxazole (5.2 g) was added dropwise with energetic stirring to a hot solution of sodium bromide (10.0 g) in aqueous methanol, and the mixture was boiled for 2 hours. The precipitate of sodium chloride was filtered off, acetone was added to the filtrate until it clouded, and the mixture was warmed for a further 1 hour. The mixture, after cooling, was diluted with four times its volume of water, the oil that separated was extracted with ether, the extract was dried over magnesium sulfate, the ether was driven off, and the residue was vacuum-distilled. Yield 5.1 g (71% of theoretical). After redistilling the substance has the following constants: b.p. 58-60° at 7 mm; n_D^{20} 1.4878.

Found %: N 8.72; 8.67
C_4H_4ONBr. Calculated %: N 8.58

Bromomethylisoxazole is a colorless heavy oil with a sharp odor and lachrymatory effect; it is fairly stable.

IX. 3-Iodomethylisoxazole

3-Chloromethylisoxazole (5.1 g) was added to a solution of 11.0 g of sodium iodide in 40 ml of dry acetone, and the reaction mixture was allowed to stand in the dark for 4 hours. The precipitate of sodium chloride was filtered off (weight 2.38 g; according to theory: 2.59 g), and the filtrate was diluted with three times its volume of water. The heavy oil that came out was separated, washed with a thiosulfate solution, and dried over calcium chloride in the dark. Yield of crude product 8.3 g (92% of theoretical). For purification purposes, the substance may be distilled only in small portions; it then has the following constants: b.p. 96-100° at 1-2 mm; n_D^{20} 1.5700.

Found %: N 7.17
C_4H_4ONI. Calculated %: N 6.60

Iodomethylisoxazole is a heavy oil with a sharp odor; it rapidly darkens on storing.

X. 3-Isoxazole-acetonitrile

3-Chloromethylisoxazole (9.0 g) in 30 ml of alcohol was added to a hot solution of sodium cyanide (12.0 g) in 5 ml of water, and the mixture was heated on the water bath for 2 hours. The mixture, after cooling, was diluted with three times its volume of water and repeatedly extracted with ether. The extract was dried over magnesium sulfate, the ether was driven off, and the residue was vacuum-distilled. Yield 2.8 g (34% of theoretical). After repeated distillation, the substance had the following constants: b.p. 91-92° at 4 mm; d_4^{20} 1.2095; n_D^{20} 1.4751.

Found %: N 26.20

$C_5H_4ON_2$. Calculated %: N 25.94

3-Isoxazole-acetonitrile is a colorless liquid of characteristic odor. It rapidly darkens on keeping.

SUMMARY

1. Alkylisoxazoles are prepared by the reaction of β-chlorovinyl ketones with hydroxylamine. This reaction can be used as a preparative method for synthesizing isoxazoles.

2. It is shown that the substances obtained are mixtures of the isomeric α- and γ-alkylisoxazoles.

3. It is shown that the chlorine atom in 3-chloromethylisoxazole is very readily replaced and may be exchanged for bromine, iodine, and the cyanide group.

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SYNTHESIS OF AROMATIC ORGANO-ANTIMONY COMPOUNDS

BY THE AID OF ARYLAZOFORMATES

O. A. Reutov and O. A. Ptitsyna

A method has been developed by one of us in conjunction with A.N.Nesmeyanov for the synthesis of aromatic organo-mercury compounds by the reaction of potassium arylazoformates with mercuric chloride in acetone medium [1]:

$$ArN_2CO_2K + HgCl_2 \rightarrow ArHgCl + N_2 + CO_2 + KCl$$
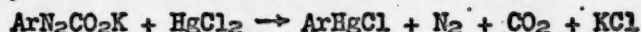
In the present work, this method is extended to the synthesis of organo-antimony compounds.

It was found that arylazoformates react readily with antimony trichloride in the cold, both in ethyl acetate and in acetone, giving the corresponding organo-antimony compounds. These were formed, for example, by the reaction of antimony trichloride with the potassium salts of phenylazoformic, p-tolylazoformic, p-bromophenylazoformic, p-nitrophenylazoformic, and β-naphthylazoformic acids. In the reaction of potassium 2,4,6-tribromophenylazoformate with antimony trichloride only 1,3,5-tribromobenzene is formed, and the monopotassium salt of p-sulfophenylazoformic acid does not react at all with antimony trichloride. The separation of the organo-antimony compounds formed was effected by converting them into the corresponding oxides and arylstibonic acids. The results are given in Table 1.

It will be seen from Table 1 that the total yield of organo-antimony compounds is fairly high. The main reaction products are aromatic stiboso compounds (generally prepared by the decomposition of the double diazonium salts [2]) and arylstibonic acids (generally prepared by the Bart-Schmidt reaction [3]). In certain cases (Experiments 1 and 4) double diazonium salts are formed also.

The formation of aromatic stiboso compounds probably proceeds as follows:

$$Ar-N=N-C{\overset{O}{\underset{OK}{}}} + SbCl_2 \rightarrow ArSbCl_2 + N_2 + CO_2 + KCl;$$

$$ArSbCl_2 \xrightarrow{H_2O} ArSbO.$$
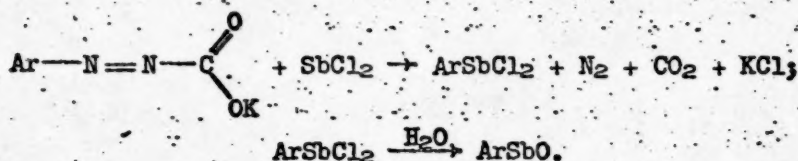
In the formation of arylstibonic acids, as also in the Bart-Schmidt reaction, antimony changes its valency (from three to five). In view of the fact that in several of the reactions we investigated May's salts were isolated, it may be supposed that the formation of arylstibonic acids may proceed through the double diazonium salt stage:

$$ArN_2Cl \cdot SbCl_3 \rightarrow ArSbCl_4 + N_2;$$

$$ArSbCl_4 \xrightarrow{H_2O} ArSbO(OH)_2.$$
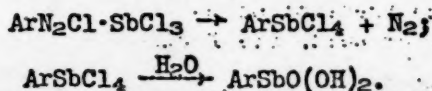
TABLE 1
Reaction of Arylazocarboxylates with Antimony Trichloride

No.	Arylformate	Temperature of reaction (°C)	Amt. of solvent (ethyl acetate), ml	Excess $SbCl_3$ (%)	Reaction products (%)			
					$ArSbO(OH)_2$	$ArSbO$	$(Ar_2Sb)_2O$	Double salt $ArN_2Cl \cdot SbCl_3$
1	$C_6H_5-N=N-C\begin{smallmatrix}O\\OK\end{smallmatrix}$	60-70	120	50	–	27	–	16
2	$p-CH_3C_6H_4-N=N-C\begin{smallmatrix}O\\OK\end{smallmatrix}$	16-18	120	50	11.5	44	–	–
3	$p-O_2NC_6H_4-N=N-C\begin{smallmatrix}O\\OK\end{smallmatrix}$	16-18	120	50	50.7	–	–	–
4	$p-BrC_6H_4-N=N-C\begin{smallmatrix}O\\OK\end{smallmatrix}$	16-18	120	50	53.8	–	10.3	18
5	$\beta-C_{10}H_7-N=N-C\begin{smallmatrix}O\\OK\end{smallmatrix}$	16-18	120	50	–	90	–	–

The mechanism of the formation of the double diazonium salts[1] was investigated in detail. We found that antimony pentachloride, like the trichloride, reacts energetically in the cold with potassium phenylazoformate according to the equation:

$$C_6H_5-N=N-C\begin{smallmatrix}O\\OK\end{smallmatrix} + SbCl_5 \rightarrow C_6H_5-\overset{+}{\underset{N}{\overset{\|}{N}}}SbCl'_4 + CO_2 + KCl ,$$
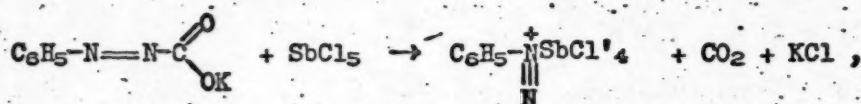
giving the double diazonium salt in 76% yield.

In connection with this, the suggestion wa made that the formation of May's salt in the reaction of potassium phenylazoformate with antimony trichloride may be associated with the presence in the latter of antimony pentachloride. However, this suggestion was found to be incorrect, for antimony trichloride that had been distilled over metallic antimony (and was consequently free from $SbCl_5$) gave May's salt in the reaction with $C_6H_5N_2CO_2K$ with the same yield as that given by undistilled $SbCl_3$.

The following scheme:

$$C_6H_5N_2CO_2K \xrightarrow{SbCl_3} C_6H_5N_2COCl \rightarrow C_6H_5N_2Cl + CO$$
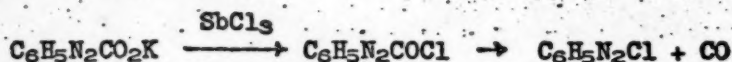
[1] It should be noted that in the reaction of potassium arylazoformates with mercuric chloride no double diazonium salts are formed.

was also rejected on the grounds that in the reaction investigated no trace of carbon monoxide is formed.

The further suggestion was made that the formation of double diazonium salts is associated with the reduction of antimony trichloride to compounds of lower valency (in particular, to metallic antimony):

$$3C_6H_5N_2CO_2K + 3SbCl_3 \rightarrow 3C_6H_5N_2CO_2SbCl_2 + 3KCl$$
$$3C_6H_5N_2CO_2SbCl_2 \rightarrow 3C_6H_5N_2Cl + 3CO_2 + SbCl_3 + 2Sb$$
$$3C_6H_5N_2Cl + 3SbCl_3 \rightarrow 3C_6H_5-\overset{+}{N}SbCl_4$$
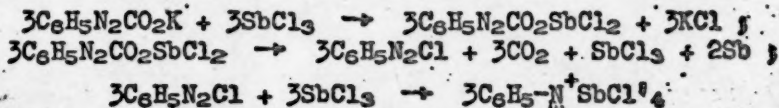
However, such a mechanism is contradicted by the non-formation of metallic antimony in the reactions investigated.

In further investigations it was remarked that the oxygen of the air takes part in the process of the formation of the double diazonium salt. Thus, if immediately after setting on the reaction of ArN_2CO_2K with $SbCl_3$ the reaction mixture is isolated from the air, then the double diazonium salt is not formed even after many days. In control experiments, in which air is not excluded, the double diazonium salt is formed in the course of a few hours. If the reaction mixture that has been preserved for a long time out of contact with the air (and therefore does not contain any double diazonium salt) is brought into the air in an open vessel, then in a few hours $ArN_2Cl \cdot SbCl_3$ is formed. If finally, the reaction of ArN_2CO_2K with $SbCl_3$ is carried out in ethyl acetate at low temperature[1] with simultaneous passage of air, then the double diazonium salt crystallizes straight out of solution.

On the basis of the facts given above we came to the conclusion that the reaction leading to the formation of $ArN_2Cl \cdot SbCl_3$ is as follows:

1. $Ar-N{=}N-COOK + SbCl_3 \rightarrow Ar-N{=}N-COOSbCl_2 + KCl$.

The compound formed is only partially decomposed at an early stage of the reaction according to the equation:

$$ArN_2CO_2SbCl_2 \rightarrow ArSbCl_2 + N_2 + CO_2.$$
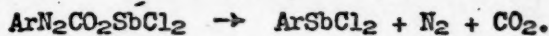
This is confirmed by the observation that at the beginning not more than half of the theoretical amounts of CO_2 and N_2 is evolved.

2. The remaining part of the substance $ArN_2CO_2SbCl_2$[2] decomposes on standing, only in presence of the oxygen of the air, giving the double diazonium salt:

$$2Ar-N{=}N-\overset{\overset{\textstyle O}{\|}}{C}-OSbCl_2 + 2SbCl_3 + O_2 \rightarrow 2ArN_2Cl \cdot SbCl_3 + 2CO_2 + 2SbOCl.$$
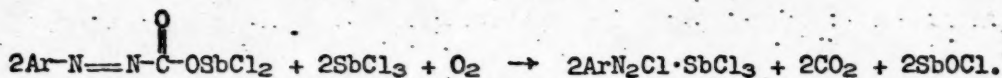
It should be noted that among the products isolated in the reaction of $C_6H_5N_2CO_2K$ with $SbCl_3$ in acetone and in ethyl acetate was the double salt of benzenediazonium chloride not with $SbCl_3$, but with Sb_2O_3. This "anomalous double

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[1] A low temperature was used in order to slow down the reaction between potassium arylazoformate and antimony trichloride.

[2] It is possible that the variable stability of the $C_6H_5N_2CO_2SbCl_2$ molecules is associated with cis-trans isomerism.

salt" is decomposed, like the normal May's salt, with Zn and Cu powder. In the reaction in toluene, only the normal double salt is formed.

The "anomalous double salt" is evidently formed as a result of the hydrolysis of the normal double salt by the moisture of the air during the evaporation of the solvent (and in certain cases — during the treatment of the reaction products with 5 N hydrochloric acid.

This supposition is confirmed by the formation of $C_6H_5N_2Cl \cdot Sb_2O_3$ from a known specimen of $C_6H_5N_2Cl \cdot SbCl_3$ on hydrolyzing the latter substance in acetone solution.

The reaction of potassium phenylazoformate with antimonytrichloride was studied by us in detail.

The experimental results are given in Table 2

TABLE 2

Reaction between Potassium Phenylazoformate and Antimony Trichloride under Various Conditions

No.	Solvent	Temperature, °C		Solvent (ml)	Excess SbCl₃ %	Reaction products, %			Double diazonium salt
		of reaction	at which solvent distills off			$(C_6H_5)_2SbO_2H$	C_6H_5SbO	$[(C_6H_5)_2Sb]_2O$	
1	$CH_3CO_2C_2H_5$	16–18	30–35	120	50	13.1	-	-	-
2	$CH_3CO_2C_2H_5$	60–70	30–35	120	50	26.3	-	-	-
3	CH_3COCH_3	16–18	16–18	120	50	32	-	-	15.3
4	CH_3COCH_3	50	16–18	120	100	20.3	-	-	20
5	$CH_3C_6H_5$	16–18	16–18	120	50	-	-	-	10
6	$CH_3C_6H_5$	16–18	16–18	120	200	-	-	-	45
7	CH_3COCH_3	16–18	16–18	120	200	9	-	-	45
8	CH_3NO_2	16–18	35–40	60	50	9	-	-	-
9	Petroleum ether	50–60	16–18	200	50	-	-	-	10
10	$CH_3CO_2C_2H_5$	60–70	16–18	200	50	-	27	-	16

On the basis of these results, the following conclusions may be made:

1. The optimum conditions for the preparation of diphenylstibinic acid consist in the use of acetone as solvent, the carrying out of the reaction at room temperature, and the use of 50% excess of antimony trichloride (expt. 3).

2. Acetone and ethyl acetate are the most suitable solvent for use in the preparation of diphenylstibinic acid.

3. The greatest yield of double diazonium salt is obtained by using a twofold excess of antimony trichloride.

The only difference in conditions between expt. 2 and expt. 10 is that in the first case the solvent is driven off at 30-35°, whereas in the second case it is evaporated off at room temperature. Nevertheless, the reaction products in these experiments are different. This circumstance led us to the idea that chloro-diphenylstibinedichloride may be formed as a result of reaction between dichloro-phenylstibine and May's salt, which may occur on heating during the removal of solvent:

$$C_6H_5SbCl_2 + C_6H_5-\overset{+}{\underset{\parallel}{N}}SbCl'_4 \rightarrow (C_6H_5)_2SbCl_3 + N_2 + SbCl_3 .$$
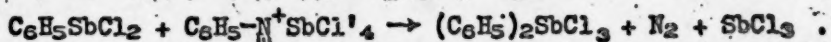
If this supposition is correct, then addition of May's salt to the reaction mixture of expt. 10, followed by heating to 30-35° should raise the yield of diphenylstib-inic acid. Experiment confirmed our supposition: the yield of diphenylstibinic acid rose from 26.3 to 37.5%. We performed also a direct proof of the formation of chlorodiphenylstibine dichloride in the reaction of $C_6H_5SbCl_2$ with $C_6H_5N_2SbCl_4$.

May's salt was first decomposed by zinc dust under the conditions used in the method for the synthesis of organo-antimony compounds by way of double diazonium salts [2]. The inorganic precipitate was filtered off, and to the filtrate, warmed to 50-60°, May's salt was again added. When gas evolution had stopped, the mixture was warmed for some time at 30-35°. In this case the only reaction product was diphenylstibinic acid.

The reaction can be expressed by the scheme:

$$3C_6H_5N_2Cl\cdot SbCl_3 + Zn \xrightarrow{CH_3CO_2C_2H_5} [C_6H_6 + ClCH_2CO_2C_2H_5]^{1)} +$$
$$+(C_6H_5)_2SbCl_3 + 2 SbCl_3, + ZnCl_2 + 3N_2 .$$
$$\downarrow H_2O$$
$$(C_6H_5)_2SbOOH\cdot Sb_2O_3{}^{2)}$$
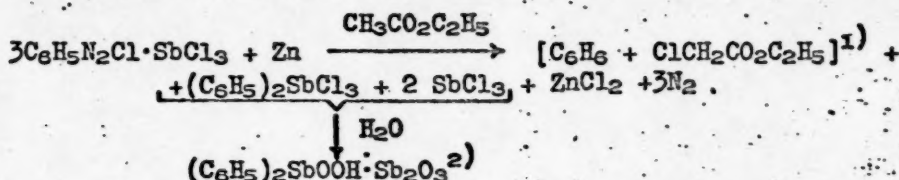
We have therefore succeeded in directing the decomposition of the double diazonium salt so that, instead of a mixture of products, a single substance $(C_6H_5)_2SbOOH\cdot Sb_2O_3$ is formed, this substance being, at the same time, one that is not formed at all by the diazo method. This method of preparing diphenyl-stibinic acid is the most suitable preparative synthesis for this substance. In the reaction of $C_6H_5N_2CO_2K$ with $SbCl_3$ in acetone, diphenylstibinic acid is again formed, evidently from dichlorophenylstibine and May's salt.

As was shown by Bruker [4], the complex $C_6H_5SbCl_2\cdot C_6H_5N_2Cl$ decomposes spon-taneously in acetone. Taking this into consideration, the fact that we isolated diphenylstibinic acid from acetone solution even when carrying out the reaction and treatment of the reaction mixture at room temperature can be understood.

EXPERIMENTAL

1. Reaction between Potassium Phenylazoformate and Antimony
Trichloride in Ethyl Acetate

Potassium phenylazoformate (10 g) (preparation, see [5] and [6]) was sprinkled with stirring into a solution of 17.7 g of antimony trichloride

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1)The products indicated by the square brackets were not identified.

2)In the synthesis of diphenylstibinic acid, both by way of arylazoformates and by way of double diazonium salts, it was obtained in the form of a complex with antimony oxide $(C_6H_5)_2SbOOH\cdot Sb_2O_3$

(50% excess) in 120 ml of ethyl acetate at 60-70°. Stirring was continued for a further 30 min. The inorganic precipitate that came out (8 g) was filtered off and washed with ethyl acetate. The washings were united with the filtrate, and the ethyl acetate was driven off in a vacuum at 30-35°. The viscous mass that remained was washed twice with cold 5 N HCl (30 and 15 ml) to remove inorganic antimony compounds. To the washed residue, five times its volume of 96% alcohol was added. The alcoholic solution was poured in a thin stream with stirring into an excess of 5% ammonia containing a large quantity of ice. The yellowish precipitate that was then formed was filtered off and washed with alcohol and ether. Yield of $(C_6H_5)_2SbOOH \cdot Sb_2O_3$ 4.1 g (26.3% of theoretical).

Analysis for antimony in this and all following experiments was carried out by decomposing a weighed amount of the substance with concentrated sulfuric acid and permanganate, decolorizing the mixture obtained with hydrochloric acid, reducing the quinquevalent antimony formed into tervalent by the aid of potassium iodide, and titrating the iodine liberated with 0.1 N sodium thiosulfate [7,8].

<div align="center">

Found %: Sb 60.73

$(C_6H_5)_2SbOOH \cdot Sb_2O_3$. Calculated %: Sb 60.85

</div>

On passing hydrogen sulfide through a hydrochloric acid solution of the substance obtained, an orange precipitate of antimony sulfide is formed, whereas, under these conditions, a known sample of pure diphenylstibinic acid gives a white precipitate. On mixing a hydrochloric acid solution of the substance obtained with a solution of pyridine in hydrochloric acid, a complex of chlorodiphenylstibine dichloride and pyridine is precipitated; it melts with decomposition at 263-264°. Data in literature: Pfeiffer and Schmidt [8], m.p. 265°.

On dissolving $(C_6H_5)_2SbOOH \cdot Sb_2O_3$ in hot 5 N HCl, chlorodiphenylstibine dichloride, m.p. 175.5-176°, is obtained. Data in literature: Morgan and Micklethwait [9], m.p. 176°; Schmidt [10], m.p. 175°; Bruker [4], m.p. 171-172°.

<div align="center">

Found %: C 37.78; H 3.12

$(C_6H_5)_2SbCl_3$. Calculated %: C 37.70; H 2.64

</div>

If in the treatment of the reaction mixture ethyl acetate is not driven off, but is caused to evaporate at room temperature, then the "anomalous double salt" (16% of theoretical) and stibosobenzene (27% of theoretical) are obtained.

2. Reaction of Potassium Phenylazoformate with Antimony Trichloride in Acetone

Potassium phenylazoformate (10 g) is sprinkled over a period of 20 min. into a solution of 17.7 g of antimony trichloride (50% excess) in 120 ml of acetone with stirring, which is continued a further 30 min. The inorganic precipitate that forms is filtered off and washed with acetone. The solvent is evaporated off from the filtrate at room temperature. The residual viscous mass is washed twice with 5N HCl. To the washed residue, five times its volume of 96% alcohol is added, and the solution is cooled with snow and salt. A powdery precipitate of violet color is formed. The substance is decomposed by copper powder in acetone; it has no definite melting point.

<div align="center">

Found %: Sb 56.40

$C_6H_5N_2Cl \cdot Sb_2O_3$. Calculated %: Sb 56.50

</div>

Yield of "anomalous double salt" 3.5 g (15.2% of theoretical). The

alcoholic filtrate is poured into an excess of 5% ammonia containing a large amount of ice. The yellow precipitate that forms is washed with alcohol and several times with ether. Yield of $(C_6H_5)_2SbOOH \cdot Sb_2O_3$ 5 g (32% of theoretical).

$$\text{Found } \%: \text{ Sb } 60.56$$
$$(C_6H_5)_2SbO_2H \cdot Sb_2O_3. \text{ Calculated } \%: \text{ Sb } 60.85$$

The substance obtained is converted into chlorodiphenylstibine dichloride, m.p. 174-175°. Data in literature: Schmidt [10], m.p. 175°.

From the ether used for washing $(C_6H_5)_2SbO_2H \cdot Sb_2O_3$, 0.25 g of bis(diphenylantimony) oxide (1.6% of theoretical) was isolated; it was identified in the form of diphenylantimony acetate, m.p. 132°. Data in the literature: Schmidt [10]; m.p. 132°; Talalaeva [11], m.p. 133°.

3. Reaction of Potassium Phenylazoformate with Antimony Trichloride in Toluene

Potassium phenylazoformate (4 g) was sprinkled over a period of 20 min. at room temperature into a solution of 15.6 g of antimony trichloride (three-fold excess) in 120 ml of toluene with stirring, which was continued for a further 20 min. The reaction mass thickened up. The precipitate was filtered off, well washed with cold 5 N HCl, and then washed with alcohol. The substance obtained melted at 82-83°, which corresponds to May's salt.

$$\text{Found } \%: \text{ N } 7.46$$
$$C_6H_5N_2SbCl_4. \text{ Calculated } \%: \text{ N } 7.60$$

Yield of May's salt 3.5 g (45% of theoretical). In this experiment no organo-antimony compounds were formed.

4. Reaction of Potassium p-Tolylazoformate with Antimony Trichloride

Potassium p-tolylazoformate (10 g) was sprinkled over a period of 20 min. at room temperature into a solution of 17 g of antimony trichloride (50% excess) in 120 ml of ethyl acetate with stirring, which was continued for a further 30 min. The inorganic precipitate was filtered off (6.5 g), and the filtrate evaporated down at room temperature. The further treatment was as in Experiment 2. 1.7 g (11.5% of theoretical) of p-tolylstibonic acid was separated from alcohol solution in the form of the oxychloride.

$$\text{Found } \%: \text{ Sb } 40.21$$
$$CH_3C_6H_4SbOCl_2. \text{ Calculated } \%: \text{ Sb } 40.58$$

$p\text{-}CH_3C_6H_4SbOCl_2$ is a powder, insoluble in organic solvents apart from glacial acetic acid; it forms a complex with pyridine. From ammoniacal solution there was obtained 4.9 g (44% of theoretical) of p-stibosotoluene.

$$\text{Found } \%: \text{ Sb } 53.3$$
$$CH_3C_6H_4SbO. \text{ Calculated } \%: \text{ Sb } 53.21$$

5. Reaction of Potassium p-Nitrophenylazoformate with Antimony Trichloride

Potassium p-nitrophenylazoformate (10 g; preparation, see [12]) was sprinkled over a period of 20 min. at room temperature into a solution of 14.7 g (50% excess) of antimony trichloride in 120 ml of ethyl acetate with stirring, which was continued for a further 30 min. The inorganic precipitate (5.7 g) was filtered off, and the filtrate, after evaporating off the ethyl acetate, was treated as in Experiment 2. From the alcohol solution, a precipitate (2.5 g) that contained no antimony came down (it was not investigated further). On pouring the alcoholic solution into ammonia, 6.8 g (50.7% of theoretical) of p-nitrophenylstibonic acid was obtained:

Found. %: Sb 38.98

$O_2NC_6H_4SbO_3H_2$. Calculated %: Sb 39.01

6. Reaction of Potassium p-Bromophenylazoformate with Antimony Trichloride

Potassium p-bromophenylazoformate (5.3 g; preparation, see [12]) was sprinkled over a period of 15 min. at room temperature into a solution of 7.4 g of antimony trichloride (50% excess) in 120 ml of ethyl acetate with stirring, which was continued for a further 30 min. The precipitate formed (2.5 g) was filtered off and washed with ethyl acetate and with cold 5 N HCl. The substance that remained after washing with hydrochloric acid (1.6 g) melted at 112-113° with decomposition; on adding copper powder in acetone, it decomposed with evolution of nitrogen. The substance is a double salt of p-bromobenzenediazonium chloride with $SbCl_3$. Yield 1.6 g (18% of theoretical). Data in literature: Nesmeyanov [13], m.p. 113°.

The ethyl acetate filtrate was treated as in Experiment 2. A precipitate was obtained from alcohol (0.85 g), which was decomposed by copper powder in acetone, but did not have the melting point characteristic for the double salt of p-bromobenzenediazonium salt with $SbCl_3$ (it was not investigated further). On pouring the alcoholic solution into ammonia, 3.5 g of p-bromophenylstibonic acid (53.8% of theoretical) was obtained.

Found %: Sb 36.48

$BrC_6H_4SbO(OH)_2$. Calculated %: Sb 36.59

From the ethereal solution obtained from washing the precipitate produced by ammonia with ether, bis[bis(p-bromophenyl)]antimony oxide was isolated; it was identified in the form of bis(p-bromophenyl)antimony acetate; m.p. 131-132°. Data in the literature: Nesmeyanov [13], m.p. 131-132°; Blicke [14], m.p. 132°.

7. Reaction of Potassium β-Naphthylazoformate with Antimony Trichloride

In the reaction of potassium β-naphthylazoformate (obtained by hydrolysis of the ethyl ester of β-naphthylazoformic acid) with antimony trichloride under the conditions of the previous experiment, β-stibosonaphthalene is formed with a 90% yield. The substance becomes rapidly disproportionated so that, even after reprecipitation, analysis does not give satisfactory results.

Found %: Sb 48.17

$C_{10}H_7SbO$. Calculated %: Sb 46.06

8. Reaction of Potassium Phenylazoformate with Antimony Pentachloride

Potassium phenylazoformate (4 g) is sprinkled at room temperature with stirring into a solution of 7.8 g of antimony pentachloride (25% excess) in 125 ml of toluene. The reaction mixture becomes thick. The precipitate is filtered off and washed with toluene, cold 5 N HCl, and alcohol. The May's salt produced melts at 82-83°. Known May's salt melts at 82-83°, and a mixed test shows no depression. Yield 6 g (76% of theoretical).

9. Reaction of Potassium Phenylazoformate with a Three-Fold Excess of Antimony Trichloride in Acetone

3.5 g of potassium phenylazoformate, reacted under the usual conditions with 12.6 g of antimony trichloride in 125 ml of acetone yielded 3 g of May's salt (45% of theory) and 0.5 g $(C_6H_5)_2SbOOH \cdot Sb_2O_3$ (9% of theory).

10. Reaction of Potassium Phenylazoformate with
Antimony Trichloride with Addition of May's Salt

Potassium phenylazoformate (5 g) is sprinkled with stirring into a solution of 8.8 g of antimony trichloride (50% excess) in 120 ml of ethyl acetate at 60-70°. May's salt (12 g) is then added, and the reaction mixture is warmed on the water-bath at 35-40° for 40 min. The inorganic precipitate and the unchanged May's salt are filtered off. The filtrate is treated as in Experiment 2. No precipitate is obtained from alcohol. On pouring the alcoholic solution into ammonia, the complex $(C_6H_5)_2SbOOH \cdot Sb_2O_3$ is obtained. Weight, 2.9 g (37.5% of theoretical).

Found %: Sb 60.77
$(C_6H_5)_2SbO_2H \cdot Sb_2O_3$. Calculated %: Sb 60.85

11. Preparation of the Double Salt of Benzenediazonium Chloride
and Antimony Oxide ("Anomalous" Double Salt)

Authentic May's salt (0.5 g) is dissolved in 50 ml of acetone, and water (3 ml) is added to the solution. A white powdery precipitate is formed, which is decomposed by copper powder in acetone, but does not melt on heating up to 185° (authentic May's salt melts at 82-83°).

12. Preparation of Diphenylstibinic Acid
by the Double Diazonium Salt Method

May's salt (10 g) is decomposed by 2.5 g of zinc dust in 50 ml of ethyl acetate, previously heated to 60°. The inorganic precipitate is filtered off, and to the filtrate, heated to 60°, May's salt (5 g) is added. There is a vigorous reaction; all the May's salt dissolves in 10-15 min. The solution is heated for 30 min. at 30-35° on a water-bath. The solvent is evaporated off, and the further treatment is carried out as in Experiment 2. May's salt precipitates from alcohol (2.2 g). From ammonia, the complex of diphenylstibinic acid with antimony trioxide is separated (4.2 g, 60.4% of theoretical).

Found %: Sb 60.46
$(C_6H_5)_2SbO_2H \cdot Sb_2O_3$. Calculated %: Sb 60.85

SUMMARY

1. A method has been developed for the synthesis of aromatic organo-antimony compounds by way of arylazoformates.

2. A mechanism has been proposed for the reactions considered.

3. It has been found that, under the action of antimony tri- or penta-chloride, arylazoformates may be converted into aromatic diazonium salts.

4. A convenient preparative method is proposed for the production of diphenylstibinic acids, which are not readily accessible; it consists in the decomposition of the double salt of benzenediazonium chloride and antimony trichloride by means of zinc.

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INVESTIGATIONS RELATING TO β-AMINO ACIDS

SYNTHESIS AND REACTIONS OF β-AMINOBUTYRIC ACID

V. M. Rodionov and N. G. Yartseva

Although β-aminobutyric acid has been known for a long time [1,2] and many investigators have prepared both the acid, and also a number of its derivatives [3,8] information concerning its reactions is nevertheless still rather scanty. At the same time, this acid is undoubtedly worthy of attention and of thorough comprehensive study as a substance of high physiological activity. As early as 1899 there are indications in the literature that this acid has an effect on the activity of the heart and on the breathing [9,10].

Experiments carried out at our request by Shchepkin, for which we express here our deep gratitude, fully confirmed the earlier observations and clearly showed that, on injection under the skin of a dog, a 0.1% solution of β-amino-butyric acid produces a great increase in blood pressure and an appreciable increase in pulse rate and a more concentrated solution (1%) rapidly produces complete stoppage of the action of the heart. It is very probable that further study of the reactions of β-aminobutyric acid may lead to the discovery of new physiologically active preparations and, possibly, of new medicinal preparations.

The absence of a readily accessible method of preparing β-aminobutyric acid was doubtless one of the obstacles in the way of the study of its reactions. In our investigations, we have used a method developed some time ago in our laboratory for the preparation of this acid [11-14], and we carried out the synthesis according to the scheme below, the β-amino acid required being separated from the reaction mixture by way of the lead salt:

in the precipitate   in the solution.

β-aminobutyric acid

However, owing to the very high solubility of β-aminobutyric acid in water (1 g in 1 g of water) and also owing to the high volatility and great tendency to polymerization of the original acetaldehyde, we did not succeed in obtaining yields of greater than 23%. The original method was therefore modified in the following way: 1) instead of introducing a mixture of acetaldehyde and ammonia into the condensation reaction with malonic acid, previously prepared aldehyde-ammonia was used; 2) the reaction was carried out in the presence of a catalyst (trimethylphenylammonium hydroxide); and 3) the condensation product was converted directly into the less soluble benzoyl derivative, without prior separation of the amino acid in the pure state. In this way, the yield was increased to 36% (Table 1).

TABLE 1

| Experiment No. | Yield (%) | |
	With catalyst	Parallel experiment without catalyst
1	17	–
2	17.97	–
3	22.5	14.4
4	18.73	13.7
5	26.7	–
6	36.4	–
7	34.8	14.26
8	36.1	–
9	–	15.01 (with sodium ethoxide)

TABLE 2

| Experiment No. | Yields of β-benzamido-β-furylpropionic acid (%) | | Yield of furylacrylic acid (%) | |
	With catalyst	Without catalyst	With catalyst	Without catalyst
1	11.48	–	6.2	–
2	–	7.4	–	–
3	13.4	–	41.8	–
4	9.4	5.3	34.8	–

As our catalyst always contains a certain amount of sodium ethoxide, one experiment was carried out with ethoxide, but without catalyst; the yield was considerably less. In order to confirm the effect of the catalyst, four experiments were carried out in an analogous way with furfuraldehyde:

β-benzamido-β-furylpropionic acid

In Table 2 the yields of the β-benzamido-β-furylpropionic acid and furylacrylic acid prepared in this way are given.

In all the experiments carried out with the catalyst, the condensation product was less resinified, the acid was easier to purify, and the yield was greater.

The suggestion that β-aminobutyric acid could be obtained by the hydrolysis of the benzoyl derivative was not found to be feasible. The benzoyl group does not split off on boiling for 6 hours with 20% HCl, with 10% KOH, or with glacial acetic acid containing HCl. β-Aminobutyric acid prepared through the lead salt is very hygroscopic; it melts with decomposition at 186-187°. Determination of melting point is not reliable as a criterion of its purity owing to the above-mentioned hygroscopicity and decomposition on heating. This is the explanation of the various melting points cited by different investigators; 156° — Curtius and Himler; 187-188° — Fischer and Scheibler; 193-194° — Heilbron.

In order to verify our product we prepared the following derivatives of β-aminobutyric acid; methyldihydrouracil [15], the benzoyl derivative (by Schotten-Baumann, yield 38.7%), and the copper salt. Determination of the water of crystallization in the copper salt confirmed the observation of Krebsbakh [16] that it contains two molecules of water of crystallization, and not four, as found by Engel [17].

The benzoyl derivative obtained as indicated above by the direct benzoylation of the product of the condensation of acetaldehyde-ammonia with malonic acid melted at 153-154° (according to literature, 155-155.5° [15]), and a mixed test with a sample prepared by the benzoylation of pure β-aminobutyric acid showed no depression of melting point. The solubility of the benzoyl derivative was found to be 0.2459 g per 100 g of water at 25° (according to the literature, 0.2467 [16]). In all the preparations of N-benzoyl-β-aminobutyric acid, also some crotonic acid was isolated in low yield (about 8%).

Apart from the benzoyl derivative, also carbethoxy-β-aminobutyric acid was prepared. The N-benzoyl and N-carbethoxy derivatives were converted by means of thionyl chloride into the corresponding acid chlorides, which gave, on treatment with ammonia, the amides of N-benzoyl- and of N-carbethoxy-β-aminobutyric acid:

CH₃CHCH₂CONH₂ — CH₃CHCH₂CONH₂

NHCOC₆H₅ — NHCOOC₂H₅

m.p. 199-200° — m.p. 138-140°
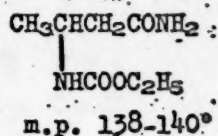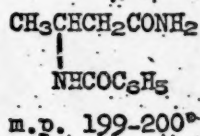
The reaction went smoothly with the benzoyl derivative, and the yield became constant (82-83%) after three experiments. For the carbethoxy compound, the yield was somewhat less (about 80%). In the preparation of β-benzamidobutyramide, a small amount of 4-methyl-6-oxo-2-phenyltetrahydropyrimidine is always formed:
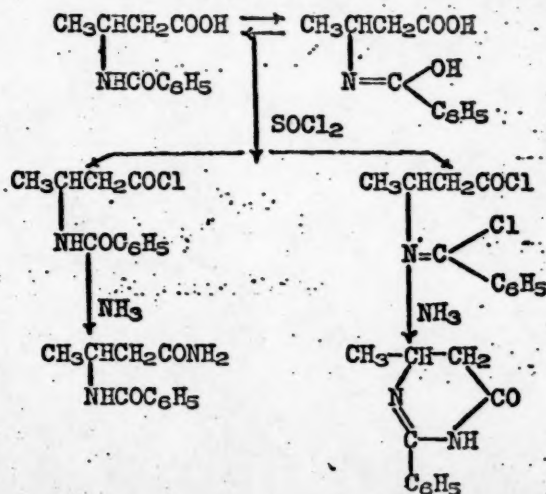
The yield of the pyrimidine depends on the amount of thionyl chloride tak[en] and on the reaction temperature. Using 2 moles of thionyl chloride per mole o[f] the initial amino acid and a temperature of 40-45°, the yield of the pyrimidin[e] did not exceed 20%, while on heating to 80°, the yield was 57%. Using 5 mole[s] of thionyl chloride at 80-82°, the yield rose to 70.6%.

As the work of Rodionov and Zvorykina (18) has shown, the amides of β-alkyl- (or aryl-) β-N-carbethoxyaminopropionic acids may be converted by alkaline hydrolysis into the corresponding β-ureido acids. On alkaline hydrolysis of β-(carbethoxyamino)-butyramide, the product was not the expected β-ureidobutyric acid, but methyldihydrouracil. It is evident that the highly water-soluble β-ureidobutyric acid could not come out of solution, as in the case of other acids, and that, on concentration of the solution, ring-closure occurred with formation of methyldihydrouracil:
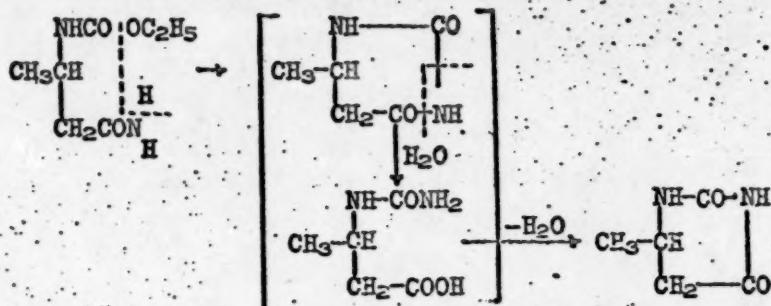
The ready ring-closure of β-ureidobutyric acid was observed by us previously in attempts to prepare this acid, following Lippich [19] and Lange and Adickes [20], by boiling β-aminobutyric acid with urea while passing a stream of air to remove ammonia (instead of nitrogen, as proposed by Lippich). Whereas β-aminopelargonic acid and β-phenyl-β-alanine gave the corresponding β-ureido acids under these conditions, β-ureidobutyric acid did not precipitate, and, on subsequent evaporation of the solution, methyldihydrouracil was obtained.

There are already several investigations that show that amides of acylated β-amino acids are converted into derivatives of imidazolidone by reaction with hypobromite [21-24]. By this reaction, β-benzamidobutyramide gave a highly water-soluble and very hygroscopic product, m.p. 86-89°. Analyses of this compound gave reason to suppose that in the reaction with hypobromite a mixture of methylimidazolidone and benzoylmethylimidazolidone is formed:

Benzoylmethylimidazolidone   Methylimidazolidone
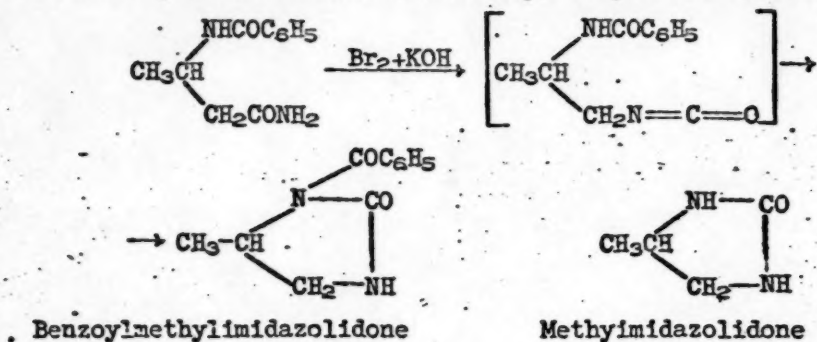
As the work of Zvorykina and Kiseleva has shown that acylimidazolidones (particularly benzoyl derivatives) are readily hydrolyzed, the substance of m.p. 86-89° was hydrolyzed with alkali. Benzoic acid was isolated, and a very hygroscopic substance of m.p. 93.5-95° (unchanged after repeated crystallization from chloroform) was obtained. Its analysis exactly corresponded to methylimidazolidone. Thus, as was to be expected, the amide of an acylated β-aminobutyric acid reacts with hypobromite in the same way as the amides of β-amino acids already investigated in this respect.

The low yield of imidazolidone suggests that under the conditions of the reaction investigated methylimidazolidone is readily hydrolyzed further to 1,2-diaminopropane:

$$CH_3-CH-CH_2 \quad CH_3-CH-CH_2$$
$$\underset{\underset{CO}{|}}{\underset{|}{NH}} \underset{NH}{|} \longrightarrow \underset{NH_2}{|} \underset{NH_2}{|}$$
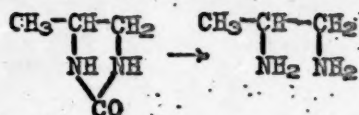
This supposition was fully confirmed, and from the reaction products, with the aid of ethyl chloroformate, the corresponding diurethan was obtained:

$$CH_3-CH-CH_2 \xrightarrow[Cl]{\overset{OC_2H_5}{\overset{|}{CO}}} CH_3-CH-CH_2$$
$$\underset{NH_2}{|} \underset{NH_2}{|} \qquad C_2H_5OOCNH \; NHCOOC_2H_5$$
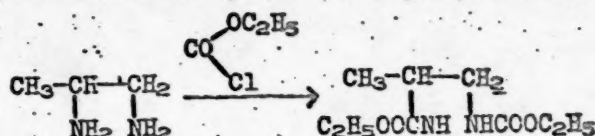
EXPERIMENTAL

1. Preparation of β-aminobutyric acid

98% Alcohol (80 ml), acetaldehyde (0.1 mole), malonic acid (0.1 mole), and an alcoholic solution of ammonia (0.11 mole) are mixed with cooling in a 250-ml conical flask. The mixture is warmed under reflux on a water-bath until bubbles of gas are evolved, which generally occurs when the temperature reaches 50-60°. Heating is continued at this temperature until the evolution of gas slows down (about 2 hr). The bath is then brought to the boil, and alcohol with traces of ammonia and aldehyde is driven off. Five hours after the start of the reaction, the water-bath is changed for an oil-bath, and heating is continued at 120° for a further 1 hour.

The reaction product is treated with hot water, transferred to a bowl, and, while stirring and heating over a gauze, PbO is added in small portions (20-25% excess over theoretical). Heating is continued until evolution of NH_3 stops. The precipitate is filtered off under suction and washed several times on the filter with hot water. The filtrate is precipitated, on cooling, with H_2S. After removing PbS, the solution is evaporated on the water-bath to a thick syrup, a few drops of absolute alcohol are added, then some ether and nuclei for crystallization. The mass is left in a desiccator over H_2SO_4, and after two or three days it all crystallizes out. It is stirred with absolute alcohol and sucked off on the funnel, where it is washed with absolute alcohol. The crystals are dried in a dessicator over H_2SO_4. Melting point 176-179°. It is purified by recrystallization from water. Melting point in a sealed capillary 186-187°. Yield did not exceed 23%.

2. Preparation of β-(Benzoylamino)-butyric Acid

a) Aldehyde-ammonia. Prepared according to Gattermann [25].

b) Catalyst (trimethylphenylammonium hydroxide). Prepared as for the preparation of β-alanine [26].

c) β-Benzamidobutyric acid. Malonic acid (10.4 g = 0.1 mole) in 30 ml of 98% alcohol is cooled in a mixture of ice and salt. Aldehyde-ammonia (6.1 g) is mixed with 30 ml of alcohol in a 250-ml conical flask, also with cooling, and the two solutions are mixed together. After stirring for 10-15 min., catalyst (5 ml) is added. The flask is then connected to a reflux condenser, and the reaction mixture is heated on a water bath to 50-60°. After about 2 hours, when the separation of gas bubbles has stopped, the bath is raised to the boil and the alcohol, with the residues of aldehyde and ammonia, is driven off. Heating is continued for 3 hr. on a vigorously boiling bath, and further heating is then given on an oil-bath at 120-130° for 1 hour.

The condensation product is a transparent yellow resin. It is dissolved with slight warming in 40-50 ml of diluted (1:1) HCl and is extracted after cooling, with ether in order to remove the unsaturated (crotonic) acid.[1]

The aqueous layer is neutralized with KOH (to Congo Red) and, after measuring its volume, is transferred to a vessel for benzoylation, which is placed in a cooling mixture. After mixing and cooling, a solution of 18 g of KOH in sufficient water to give a final concentration of 10-12% is added. When the temperature of the reacting mixture reaches +5 - 10°, benzoyl chloride (14 g = 0.1 mole) is added dropwise over an hour. Stirring is continued under cooling for one hour, and then for a further 2 hr. at room temperature. When benzoylation is complete, the solution is twice extracted with ether to remove residual benzoyl chloride and any benzamide that may be formed; the cooled and stirred solution it then precipitated with strong hydrochloric acid. β-Benzamidobutyric acid comes down in the form of a rapidly crystallizing oil. Next day, the crystals are filtered off under suction, washed on the filter with water, and dried at 70-80°. The dry substance is stirred with absolute ether to remove benzoic acid, filtered, and washed again on the filter with ether. It is recrystallized from water; m.p. 153-154°. Yield 7-8 g, i.e. 30-36% of theoretical.

Found %: C 63.43; 63.44; H 6.38; 6.31; N 6.74; 6.72
$C_{11}H_{13}O_3N$. Calculated %: C 63.76; H 6.28; N 6.76

3. Isolation of Crotonic Acid

Ether extract No. 1, after washing with water, drying over Na_2SO_4, and removal of ether, gave an oil, which distilled over between 167 and 190° and partly crystallized on standing. The thin needle-like crystals were dried on a porous plate; m.p. 71-72°; b.p. 186-189°.

Found %: C 55.22; 55.03; H 7.12; 7.21
$C_4H_6O_2$. Calculated %: C 55.81; H 6.97

The filtrate from the crystals was fractionated once again. The main fraction came over between 169 and 182°; n^{14} 1.4439. In none of the experiments did the yield of crotonic acid exceed 8%. In order to convert the cis- into the trans-form, the liquid form was heated for 2 hr. at 180° and then distilled. The main fraction came over at 185-188°. The distillate crystallized out; m.p. 70-72°.

4. Preparation of β-Benzamidofurylpropionic Acid

Furfuraldehyde (10 g) is mixed with cooling with 50 ml of absolute ether in a 250-ml flask, and the solution is saturated with dry NH_3. As much ether

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[1] Ether extract No. 1.

as possible is removed by the aid of a pump, and the residual half-solid mass of aldehyde-ammonia is mixed in the cold with 15 ml of absolute alcohol and with a cooled solution of 10.8 g of malonic acid in 35 ml of absolute alcohol. Catalyst (5 ml) is added, and the mixture is well stirred. After 10-15 min the flask is connected to a reflux condenser, and the mixture is warmed on the water-bath. At 65-70°, evolution of gas commences. This temperature is maintained until the evolution of gas bubbles slows down; the temperature is then raised to 99-100°. The total time of heating is about 5 hr. The reaction product (a dark-colored resin[1]) is treated with 100 ml of diluted (1 : 1) hydrochloric acid and is extracted with ether. After treating the ether extract with charcoal and removing the solvent, a brownish-red substance remains; after repeated dissolution in caustic potash and reprecipitation, a white crystalline powder of furylacrylic acid, m.p. 140-141°, is obtained. The hydrochloric acid solution is neutralized with caustic potash and benzoylated by adding first a solution of 18 g of KOH in 80 ml of water (total volume of liquid, 140 ml) with cooling and stirring and then 14 g of benzoyl chloride drop by drop over one hour at +5 to +10°. Stirring continues for 1 hr further in the cold and for 1 hr at room temperature. The reaction product is extracted with ether, and the aqueous layer is precipitated with strong hydrochloric acid. A crystalline precipitate of β-benzamidofurylpropionic acid (white in experiments with catalyst, gray without catalyst,is formed. Next day, it is filtered off, washed on the filter with water, dried at 70-80°, and washed with ether to remove contaminating benzoic acid. M.p. after recrystallization from water: 179-180°. The yields are indicated above.

5. Preparation of β-Benzamidobutyramide and of 4-Methyl-6-oxo-2-phenyltetrahydropyrimidine

β-Benzamidobutyric acid (10 g) is treated at 40-45° with thionyl chloride (2 moles of $SOCl_2$ per mole of acid) until bubbles of gas cease to appear. Residual $SOCl_2$ is removed in a vacuum. The acid chloride obtained is stirred in 500 ml of absolute ether, and, under cooling with ice and salt, a stream of dry NH_3 is passed, up to saturation, through the ethereal suspension. The precipitate is filtered off, washed with hot water, with 10% KOH, and again with water, recrystallized from water, and dried at 70-80°.

M.p. of β-benzamidobutyramide: 199-200°. Yield 8.2-8.34 g, i.e. 82-83% of theoretical.

Found %: C 64.88; 64.70; H 6.76; 6.82; N 13.60; 13.64
$C_{11}H_{14}O_2N_2$. Calculated %: C 64.07; 6.79 N 13.59

After driving off the solvent, light-yellow 4-methyl-6-oxo-2-phenyltetrahydropyrimidine was precipitated from the ethereal filtrate. After recrystallization from benzene it melted at 119-120°. The yields are indicated above.

Found %: N 14.58; 14.26
$C_{11}H_{12}N_2O$. Calculated %: N 14.89

6. Preparation of β-(Carbethoxyamino)-butyramide and Its Hydrolysis with 5% KOH

β-Aminobutyric acid (7 g) was dissolved in 100 ml of 11.5% aqueous KOH (3 moles). Chloroformic ester (8.5 g = 1.1 mole per mole of amino acid) was added with shaking and cooling with ice water, and the mixture was allowed to stand for 24 hr. The solution was then acidified to Congo Red and extracted with ether. The oil that remained after removing the ether crystallized out only after standing for a long time in a desiccator. The purification of the

[1] In the experiments without catalyst the product is almost black; in experiments with catalyst it is gray.

greasy crystals was very difficult. For this reason, the β-(carbethoxy)-butyric acid, of which 6.7 g was obtained, was converted without further treatment into the amide by the method described above for β-benzamidobutyramide. After recrystallization from benzene the β-(carbethoxyamino)-butyramide melted at 138-140°. Yield (5 g) 87%.

<div align="center">

Found %: N 16.51; 16.43.
Calculated %: N 16.09

</div>

0.5 g of this amide was boiled with 5 ml of KOH for half an hour over a gauze. The solution was acidified with HCl. The expected β-ureidobutyric acid was not precipitated. The mixture was evaporated to dryness and extracted with absolute alcohol. The solution was filtered and evaporated down to a syrup. It was left in a desiccator until it crystallized. The crystals were dried on a porous plate; m.p. 216-218°. A mixed test with a sample of methydihydrourcil, prepared according to E. Fischer and Röder [15], gave no depression on melting.

7. Action of Hypobromite on β-Benzamidobutyramide

Preparation of Methylimidazolidone

Starting substances:

β-Benzamidobutyramide	5.15 g	(0.025 mole)
Bromine	8 g	(2.35 ml)
KOH	11.2 g	
Water	11.5 ml	

The bromine is added dropwise to a stirred solution of KOH, cooled to -10°. The amide is then introduced in small portions at a time into the light-yellow hypobromite solution. The temperature in the mixture is 0 to +2°. At first the amide dissolves readily, but towards the end the liquid becomes opaque. After adding all the amide (2-3 hr), the flask containing the reaction mixture is immersed in a water-bath at 80°. As soon as the temperature reaches 40-55°, there is a vigorous evolution of gas, and the solution is decolorized. The flask is immediately taken off the bath, but the temperature of the mixture continues to rise and attains 65-68°. When further immersion of the flask in the 80° bath followed by its removal no longer leads to a jump in temperature, the mixture is heated at 60° for a further 10 min, and then cooled. A precipitate of amide that has not reacted (about 0.4 g) comes down. The filtrate from the removal of the amide is precipitated with hydrochloric acid (1:2). Benzoic acid is precipitated (about 76% of theoretical). As the other products of the reaction are of high solubility in water, the acid filtrate from the benzoic acid has to be evaporated down to dryness. The residue gives a reaction for nitrogen. The dry substance is extracted with chloroform (extract No. 1) and then, with warming, with 99% alcohol (extract No. 2).

Extract No. 1. After drying with Na_2SO_4 and driving off the chloroform, a mass reminiscent of petroleum jelly remained. Under the microscope, it was seen to consist of crystals impregnated with oil. On redissolving in chloroform, a very small amount of unreacted amide (0.1-0.14 g) was obtained; this was filtered off, and the filtrate was dried over Na_2SO_4. The product, after driving off the solvent, was a very hygroscopic, light-yellow substance, which turned into a powder on drying in a desiccator over P_2O_5; m.p. 86-89°. Analysis showed that this was a mixture of methylimidazolidone and benzoyl-methylimidazolidone. The amount of benzoic acid obtained also pointed to the incomplete splitting-off of the benzoyl group.

In order to obtain the pure imidazolidone, the substance of m.p. 86-89°

(1.82-1.93 g) was heated for 2 hr on the water bath under reflux with 30 ml of 20% KOH. A reddish oil came out. On acidifying and shaking repeatedly with ether, benzoic acid went over into the ether. After removal of the ether layer, the aqueous solution was evaporated down to dryness, and the dry residue was extracted with chloroform. After drying over Na_2SO_4 and removal of solvent, a substance of m.p. 93-95° was obtained. Its analysis corresponded to methylimidazolidone:

Found %: C 47.81; 48.06; H 8.0; 7.96; N 28.19; 28.15
$C_4H_8ON_2$. Calculated %: C 48.0; H 8.0; N 28.0

Extract No. 2. After driving off the alcohol, a brownish-red thick resinous mass was obtained. In order to remove residual imidazolidone, it was triturated with chloroform; the chloroform was poured off, and the residue was dissolved in 20% KOH. The solution was mixed in the cold with chloroformic ester. After 24 hr, the upper layer of the oil that was formed crystallized out. The crystals were laid out on a porous tile and then purified by repeated dissolution in ether and reprecipitation with petroleum ether. Analysis showed that this was the diurethan of propylenediamine; 1.39 g was obtained, m.p. 69-71°.

Found %: C 49.85; 49.78; H 7.91; 8.05; N 12.34; 12.36
$C_9H_{18}O_4N_2$. Calculated %: C 49.54; H 8.25; N 12.84

As was to be expected, under the conditions of the reaction with hypobromite and of the subsequent treatment, the imidazolidone is hydrolyzed with formation of propylenediamine.

SUMMARY

1. In the condensation of malonic acid with acetaldehyde-ammonia, it was found possible to increase the yield of β-aminobutyric acid, which was isolated in the form of its benzoyl derivative, up to the value of 36%, if a catalyst (trimethylphenylammonium hydroxide) was used.

2. The benzoyl group does not split off from β-benzamidobutyric acid when the latter is boiled for 6 hr with 20% HCl, or with 10% KOH, or with glacial acetic acid containing HCl.

3. As in the case of other β-amino acids studied previously, in the preparation of the amide of β-benzamidobutyric acid there is formed also the corresponding methyloxophenyltetrahydropyrimidine. The yield of the latter depends on the amount of thionyl chloride taken in the reaction of acid chloride formation and on the temperature at which this reaction is carried out.

4. When treated with hypobromite, β-benzamidobutyramide gives methylimidazolidone. Under the conditions of the reaction and of the subsequent treatment, the latter is partially hydrolyzed and is converted into propylenediamine.

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SYNTHESIS AND CHARACTERIZATION OF

β-(β-NAPHTHYL)-β-AMINOPROPIONIC ACID

AND OF CERTAIN OF ITS DERIVATIVES

Communication 1.

V. M. Rodionov and B. I. Kurtev

In previous investigations in our laboratory it has been shown that aromatic and aliphatic aldehydes readily react with malonic acid in presence of ammonia. Reaction proceeds mainly in two directions: a β-amino acid is formed, and a derivative of acrylic acid arises in a side-reaction. These reactions are as follows:

$$R(Ar)CHO + NH_3 + CH_2(COOH)_2 \rightarrow R(Ar)CH(NH_2)-CH_2COOH + H_2O + CO_2 \qquad (I)$$

$$R(Ar)CHO + CH_2(COOH)_2 \rightarrow R(Ar)CH=CHCOOH + H_2O + CO_2. \qquad (II)$$
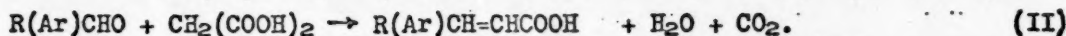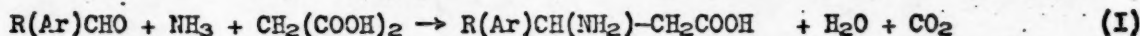
The total yield of the two readily separable substances is about 80%, 35-50% being β-amino acid. The first attempts to extend this reaction to α-naphthaldehyde led to the conclusion that in this case naphthylacrylic acid is considerably more readily formed, while the yield of β-(α-naphthyl)-β-aminopropionic acid is insignificant [1]. However, it was shown in further experiments that β-naphthaldehyde gives the β-amino acid of this series with a yield of about 60%, and recently Kravchenko [2], by changing to some extent the conditions for the condensation of α-naphthaldehyde with malonic acid, has obtained a record yield of β-(α-naphthyl)-β-alanine (more than 70%).

In order to prepare β-(β-naphthyl)-β-aminopropionic acid, it was necessary to work out a method of preparing β-naphthaldehyde. This compound was first prepared by Batterschall [3] in 1873 by dry distillation of the Ca salts of β-naphthoic and formic acids. A better yield (50%) was obtained by Chichibabin [4] by treating β-naphthylmagnesium bromide with orthoformic ester. By replacing bromonaphthalene by iodonaphthalene, Peter Sah increased the yield of β-naphthaldehyde to 70% [5]. There is a certain preparative significance in the method based on the ω-bromination of β-methylnaphthalene followed by treatment of the bromo-derivative with hexamethylenetetramine [6].

Very good yields (up to 90%) can be obtained also by the use of Stephen's method — reduction of β-naphthonitrile followed by hydrolysis [7]:

$$C_{10}H_7CN \xrightarrow[\text{ether}]{SnCl_2} C_{10}H_7CCl=NH \xrightarrow{H_2O} C_{10}H_7CHO.$$
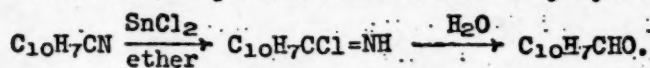
A fairly high yield (about 70-80%) is obtained also by the reduction of β-naphthoyl chloride, following Rosenmund [8]. All these methods, in spite of their high yields, are composed of many stages and give a great deal of difficulty. For this reason, an attempt was made to prepare β-naphthaldehyde by oxidizing β-methylnaphthalene with selenium dioxide. The oxidation of methyl groups in aromatic compounds to aldehyde groups has been employed on a number of occasions with great success [9].

The first experiments on the preparation of β-naphthaldehyde by this method have already been described [9]. The yield of aldehyde was only 34% of theoretical, on the basis of the β-methylnaphthalene taken. We have succeeded in almost doubling the yield of β-naphthaldehyde by using a mixture of naphthalene and methylnaphthalene (1.5:1) in the oxidative reaction. At first the reaction was carried out with mechanical stirring, but it was found later that the reaction could be carried out equally successfully by adding selenium dioxide to the mixture of naphthalene and β-methylnaphthalene heated to 220°. This method of obtaining β-naphthaldehyde, using the readily accessible β-methylnaphthalene, is the most suitable for preparative purposes. The product that we obtained melted at 60.5-61.5° and was used by us for the synthesis of β-(β-naphthyl)-β-aminopro-ionic acid, of N-(β-naphthal)-methylamine, of β-(β-naphthyl)-acrylic acid and its ester, and of β-naphthalmalonic acid (see Experimental section)..

β-(β-Naphthyl)-β-alanine, $C_{10}H_7CH(NH_2)CH_2COOH$, was first prepared by Rodionov's method. The yield (16.5%) was not very high, and variations of the basic method were therefore tried, viz. Johnson's method [10] and the method of Rodionov and Kravchenko [2]. In Johnson's method, ammonium acetate is used instead of alcoholic ammonia, and in Kravchenko's — a mixture of ammonium acetate and glacial acetic acid is used. By the use of Johnson's method, the yield of β-(β-naphthyl)-β-alanine was raised to 65%, and when we used Kravchenko and Rodionov's modification, which appears to be the most suitable for aldehydes of the naphthalene series, the yield rose to 69% of the theoretical.

When Johnson's method was used, the residue remaining after separating the amino acid was not investigated. In the remaining experiments, carried out by Kravchenko's method, the residue appeared to be almost pure β-(β-naphthyl)-acrylic acid. The formation of β-naphthalmalonic acid could not be detected in this method. The results of the experiments are given in Table 1.

TABLE 1

Method of preparation	β-(β-Naphthyl)-β-alanine (%)	β-(β-Naphthyl)-acrylic acid (%)	β-Naphthalmalonic acid (%)
a) Basic method	16	27	17
b) Johnson's method	65	The unsaturated acids were not investigated	
c) Rodionov and Kravchenko's modification	69	19	Not detected
d) In a large amount of glacial acetic acid	58.5	31	Not detected

For the characterization of β-(β-naphthyl)-β-alanine, several derivatives were prepared: 1) the methyl ester, by heating the free β-amino acid with methyl alcohol in presence of sulfuric acid; 2) the amide, by allowing the methyl ester

to stand with ammonia at room temperature for a month; 3) N-benzoyl-β-(β-naphthyl)-β-alanine; 4) N-acetyl-β-(β-naphthyl)-β-alanine and its amide and anilide; and 5) N-methyl-β-(β-naphthyl)-β-alanine. The yields and melting points of these substances are given in Table 2.

TABLE 2

Formula and name	Yield (%)	M.p. of pure substance (in °C)
$\beta-C_{10}H_7CH(NH_2)CH_2COOCH_3$ Methyl ether of β-(β-naphthyl)-β-alanine	87.5	94-95
$\beta-C_{10}H_7CH(NH_2)CH_2CONH_2$ Amide of β-(β-naphthyl)-β-alanine	64.5	143.5-144.5
$\beta-C_{10}H_7CH(NH\cdot CO\cdot C_6H_5)CH_2COOH$ N-Benzoyl-β-(β-naphthyl)-β-alanine	90.5	209-210
$\beta-C_{10}H_7CH(NH\cdot COCH_3)CH_2COOH$ N-Acetyl-β-(β-naphthyl)-β-alanine	77	177.5-178.5
$\beta-C_{10}H_7CH(NHCOCH_3)CH_2CONH_2$ Amide of N-acetyl-β-(β-naphthyl)-β-alanine	~80%	230-231
$\beta-C_{10}H_7CH(NH\cdot COCH_3)CH_2CONH\cdot C_6H_5$ Anilide of N-acetyl-β-(β-naphthyl)-β-alanine	–	296-237
$\beta-C_{10}H_7CH(NHCH_3)CH_2COOH$ N-methyl-β-(β-naphthyl)-β-alanine	49[1)] 29.5[2)]	195-195.5

[1)] Yield from β-naphthaldehyde, malonic acid, and potassium acetate in presence of glacial acetic acid.

[2)] Yield from N-(β-naphthal)-methylamine and malonic acid (see Experimental section).

EXPERIMENTAL

β-Naphthaldehyde. A mixture of 56.8 g of β-methylnaphthalene (b.p. 235-236°) and 80 g of naphthalene was heated on an oil-bath up to a temperature of 220°. Freshly activated selenium dioxide (44.4 g) was introduced into the mixture at this temperature in small portions at a time over 30-40 min. After each addition, the mixture was stirred with a glass rod, and vigorous ebullition occurred. Five minutes after adding the last portion of selenium dioxide, the reaction mixture began to boil gently. Heating was discontinued, and the cooled mixture was dissolved in ether and filtered from the black selenium powder. The residue was carefully washed with ether. The main filtrate and the washings were mixed with 150 ml of a bisulfite solution and stirred mechanically for 3 hours. A voluminous precipitate of the bisulfite compound of β-naphthaldehyde began to precipitate rapidly. After a few hours the strongly colored ethereal solution above the precipitate was carefully poured off; ether was again poured on to the precipitate, and the mixture was stirred and allowed to stand until the ether had completely separated. The latter was again poured off, and the precipitate, mixed with a fresh portion of ether, was transferred to a filter and washed on the filter with ether until the washings became completely colorless.

The aldehyde-bisulfite compound obtained in this way – it consisted of fine faintly pink scales – was introduced with stirring into a hot strong soda solution. Naphthaldehyde separated as a dark-colored oil. The whole mass was diluted with cold water and stirred. The naphthaldehyde, which rapidly crystallized, was filtered off, washed with water, and immediately steam-distilled.

The completely colorless crystalline β-naphthaldehyde was filtered off and dried at 50°. Yield 41.3 g, i.e., about 66% of theoretical; m.p. 60.5-61.5°.

N-(β-Naphthal)-methylamine. To a solution of 15.6 g of β-naphthaldehyde and 8.1 g of methylamine hydrochloride in 50 ml of alcohol a solution of 6.2 g of caustic potash in 40 ml of alcohol and 20 ml of water is added drop by drop with stirring and cooling. Crystallization rapidly sets in. After 5-6 hours the crystalline precipitate is filtered off and washed with alcohol and water. Yield 11.4 g (about 67% of theoretical); m.p. 81-82°. From the mother liquor a further 5.2 g of a strongly contaminated product, m.p. 66-74°, may be separated by adding water.

N-(β-Naphthal)-methylamine crystallizes well from gasoline (b.p. 115-135°). Glistening scales; m.p. 80.6-81.6°.

$$\text{Found \%: N 8.28; 8.50}$$
$$C_{12}H_{14}N. \quad \text{Calculated \%: N 8.28}$$

N-(β-Naphthal)-methylamine is readily soluble in alcohol, ether, benzene, and CCl_4; it is insoluble in water. It dissolves unchanged in hydrochloric acid in the cold, but is hydrolyzed on heating.

The methyl ester of β-(β-naphthyl)-acrylic acid was prepared by warming naphthylacrylic acid (2 g) in methyl alcohol (20 ml) in presence of sulfuric acid (3 g). Yield about 2 g, i.e. 94% of theoretical, m.p. 93-93.5° (after recrystallization from methyl alcohol). It consists of glistening scales.

$$\text{Found \%: C 79.02; H 5.51}$$
$$C_{14}H_{12}O_2. \quad \text{Calculated \%: C 79.25; H 5.70}$$

β-(β-Naphthyl)-β-alanine

a) Preparation by Rodionov's basic method. A mixture of 7.8 g of β-naphthaldehyde, 5.72 g of malonic acid, and 13.4 ml of a 7% solution of ammonia in absolute alcohol was heated in a flask, fitted with condenser for distillation, on the water bath for 10 hours. The dry residue in the flask weighed about 12 g. Half of the residue was ground into a fine powder and was extracted for $1\frac{1}{2}$ hours with 20 ml of hydrochloric acid (1:10) with mechanical stirring. The insoluble residue was filtered off and washed with dilute hydrochloric acid. The acid filtrate was evaporated down somewhat on the water-bath, cooled, extracted with ether several times, and then neutralized with sodium acetate. After standing for 10-12 hours, the precipitate that formed was filtered off, washed with water, with alcohol, and then with ether, and finally dried at 70-80°; m.p. 215-216° with decomposition; yield 0.85 g, i.e, only 16% of theoretical. After recrystallization from methyl alcohol, the melting point was raised to 220-221° (with decomposition).

$$\text{Found \%: C 72.11; 72.08; H 6.05; 5.95; N 6.91, 6.92}$$
$$C_{13}H_{13}O_2N. \quad \text{Calculated \%: C 72.54; \qquad H 6.09 \qquad N 6.51}$$

The residue forms colorless thick plates, almost insoluble in the cold in

water, methanol, and ethanol. It does not dissolve in acetone, benzene, or ether, but dissolves well in glacial acetic acid. It remains unchanged after long boiling with caustic soda (10%) or with conc. HCl. Investigation of the residue that is insoluble in hydrochloric acid showed that it consists essentially of β-naphthalmalonic acid (1.02 g isolated) and β-(β-naphthyl)-acrylic acid (1.31 g).

b) Preparation by Johnson's variant. β-Naphthaldehyde (15.6 g), malonic acid (10.4 g), ammonium acetate (10 g), and alcohol (25 ml) were heated for 10-11 hours on a boiling water bath. At first the mixture dissolved rapidly, and then a brisk evolution of gas set in and after 5-6 min. a voluminous precipitate was formed. In order to isolate the β-(β-naphthyl)-β-alanine, dil. HCl (60 ml, 1:5) was added, with constant stirring, to the reaction mixture. After heating for 10 min. at 70-80°, the precipitate formed was filtered off, washed on the filter three times with warm hydrochloric acid (1:5), and then washed with water. The acid filtrate together with the water washings were extracted 5-6 times with ether and neutralized with a solution of sodium acetate. The voluminous precipitate that formed was allowed to stand for some time and then filtered off and washed with water. The crude product was boiled for two hours with 100 ml of alcohol and then filtered hot. The residue on the filter was washed with alcohol and ether and was dried at 70-80°. Yield of β-(β-naphthyl)-β-alanine 14 g, i.e. about 65% of theoretical. The residue that was insoluble in hydrochloric acid was heavily contaminated naphthylacrylic acid and was not investigated in greater detail.

·c. Preparation by Rodionov and Kravchenko's variant. β-Naphthaldehyde (6 g), malonic acid (5 g = 25% excess), ammonium acetate (12 g = about 300% excess), and glacial acetic acid (20 ml) were heated on a boiling water-bath for 10 hours. The mixture went into complete solution at 85°, with vigorous gas evolution. Already after boiling for 1 hour a voluminous crystalline precipitate started to separate. When reaction was complete, water (50 ml) was added to the mixture, and the reaction mass was carefully stirred. The well cooled precipitate was filtered off and repeatedly extracted with water. · The united aqueous extracts were acidified with hydrochloric acid to Congo Red and were evaporated down almost to dryness on the water bath. The residue was treated in the way indicated above and yielded 0.52 g of β-(β-naphthyl)-β-alanine.

The water-insoluble part of the solid reaction mass was extracted with warm hydrochloric acid; the hydrochloric acid filtrate was extracted several times with ether and then evaporated to dryness on the water bath. 6.81 g of the amino acid hydrochloride (m.p. 210-212° with decomposition) was obtained. One third of the fresh hydrochloride (2.27 g) was converted into free β-amino acid. For this purpose the hydrochloride was dissolved in dilute acid, filtered from a small amount of insoluble precipitate, extracted with ether, and precipitated in the usual way with sodium acetate. After purifying by boiling with alcohol, 1.73 g of very pure β-(β-naphthyl)-β-alanine, m.p. 217-218°, was obtained. Thus, the total yield of the latter was 5.71 g, i.e. 69% of theoretical. The residue that remained after treating the reaction mass with hydrochloric acid was fairly pure β-(β-naphthyl)-acrylic acid, m.p. 206-207°. Yield 1.46 g, i.e. about 19% of theoretical.

d. On carrying out the experiment with somewhat different proportions of the components, namely with the mixture: 7.8 g of β-naphthaldehyde (0.05 mole), 5.72 g of malonic acid (0.055 mole), 5.78 g of ammonium acetate (0.075 mole), and 20 ml of glacial acetic acid, and working up as in experiment c, 5.59 g of β-(β-naphthyl)-β-alanine, i.e. 58.8% of theoretical, and 3.06 g of β-(β-naphthyl)-acrylic acid, i.e. about 31% of theoretical, were obtained.

The methyl ester of β-(β-naphthyl)-β-alanine. β-(β-Naphthyl)-β-alanine (8.6 g), methanol (80 ml), and conc. H_2SO_4 (12 ml) were heated for 4 hours on a water bath; methyl alcohol (50 ml) was then driven off. On cooling, the residue was neutralized with a soda solution. The oil that separated rapidly crystallized. The crystals were filtered off, washed with water, and then recrystallized from diluted methyl alcohol. Yield 7.39 g, i.e. about 80% of theoretical. Melting point of the ester after recrystallization from ligroin, 94-95°.

Found %: C 72.96; 73.19; H 6.66; 6.79; N 6.20; 6.16.
$C_{14}H_{15}O_2N$. Calculated %: C 73.74; H 6.60 N 6.11.

The methyl ester is formed as large glistening prisms from ligroin. It is readily soluble in alcohol, ether, benzene, acetone, and in dilute mineral acids; in ligroin it is difficulty soluble in the cold, but fairly soluble on warming. It is readily hydrolyzed on boiling with alkali to a salt of the β-amino acid. On standing for many days in ammoniacal alcoholic solution, it is converted into the amide of β-(β-naphthyl)-β-alanine. The alcoholic solution was filtered from small amounts of contamination and gave, after driving off the alcohol, an approximately 65% yield of not altogether pure amide, m.p. 142-143°. Recrystallization from water raised the m.p. to 143.5-144.5°. Analysis for nitrogen showed that the compound obtained was not quite homogeneous.

Found %: N 12.6; 12.41
$C_{13}H_{14}ON_2$. Calculated %: N 13.08

N-Benzoyl-β-(β-naphthyl)-β-alanine. β-(β-Naphthyl)-β-alanine (6.45 g) was dissolved in 150 ml of a 4% solution of caustic soda, and benzoyl chloride (4.2 ml) was added gradually from a dropping funnel to the ice-cooled solution. The solution obtained was left overnight, then filtered from the small amount of suspended matter, extracted twice with ether, and acidified with hydrochloric acid. The precipitate that immediately formed was filtered off some hours later and was washed with water. In order to remove benzoic acid, the precipitate was boiled with water, filtered off, washed with hot water on the filter, and then recrystallized from aqueous alcohol. Yield 8.65 g, i.e. 90.3% of theoretical.

N-Benzoyl-β-(β-naphthyl)-β-alanine crystallizes in fine glistening prisms (from aqueous alcohol); m.p. 209-210°. It is insoluble in water, ether, benzene, and mineral acids. It readily dissolves in alkalis, acetone, methanol, and ethanol.

Found %: C 75.46; 75.35; H 5.34; 5.21; N 4.53; 4.33
$C_{20}H_{17}O_3N$. Calculated %: C 75.22; H 5.37 N 4.39

N-Acetyl-β-(β-naphthyl)-β-alanine. Acetic anhydride (15 ml) was added from a dropping funnel to an ice-cooled mechanically stirred solution of 10.75 g of β-(β-naphthyl)-β-alanine in 160 ml of a 10% solution of caustic soda. The reaction mixture was left overnight and was then acidified with hydrochloric acid. The voluminous precipitate that immediately formed was filtered off some hours later, washed with water, and dried to constant weight. Yield 12.76 g; m.p. 164-174°. After recrystallizing once from alcohol, the acetyl derivative appeared to be quite pure and melted sharply at 177.5-178.5°. It crystallizes from alcohol in glistening colorless prisms. It dissolves readily in alkalis, acetone, methanol, and ethanol; with difficulty in water, ether, and benzene. Yield of recrystallized product 10.16 g, i.e. 77% of theoretical.

Found %: N 5.46; 5.45
$C_{15}H_{15}O_3N$. Calculated %: N 5.45

Anilide and amide of N-acetyl-β-(β-naphthyl)-β-alanine. A mixture of 7.72 g of N-acetyl-β-(β-naphthyl)-β-alanine, which was finely ground and dried in a vacuum desiccator, and 5 ml of thionyl chloride was heated on the water-bath at 40-50° until gas evolution ceased. The excess of thionyl chloride was driven off in a vacuum at 40-50°. The residue in the flask was a red, very viscous oil, difficultly soluble in absolute ether.

Anilide: A small quantity of the prepared acid chloride was treated with a small excess of aniline in ethereal solution at room temperature. The powder-like precipitate formed was filtered off and extracted successively with dilute HCl, caustic soda, and finally water. After one recrystallization from alcohol, 0.14 g of a substance of m.p. 236-237° was obtained. After a further recrystallization the product melted at 237-238°. The anilide crystallizes from alcohol in colorless prisms. It is insoluble in water, acids, alkalis, ether, and benzene; rather difficultly soluble in cold methanol, ethanol, and acetone, but dissolves more readily on heating.

<div align="center">

Found %: N 8.75; 8.60

$C_{21}H_{20}O_2N_2$. Calculated %: N 8.43

</div>

Amide. Strong aqueous ammonia (150 ml) was added to the main mass of the acid chloride. The mixture was shaken vigorously for 30 min. and then left to stand for several hours; the precipitate that had formed was then filtered off and well washed with alkali and water. The dried precipitate was ground and recrystallized from dilute alcohol. 5.66 g of amide, m.p. 255.5-227.5°, was obtained. By repeated recrystallization from a mixture of water and alcohol (5:1), constant m.p., 230-231°, was attained. The amide of N-acetyl-β-(β-naphthyl)-β-alanine crystallizes from aqueous alcohol in glistening long plates. It does not dissolve in ether or benzene; it is of rather poor solubility in methanol, ethanol, and acetone in the cold, but dissolves readily on warming; it is almost insoluble in cold water, but dissolves in hot water.

From the mother liquor, after evaporation and acidification, 0.76 g of the original β-(β-naphthyl)-β-alanine was isolated. Thus, the yield of amide calculated on the amount of β-(β-naphthyl)-β-alanine that reacted (7.72-0.76) is 5.56 g, i.e. about 80-81% of theoretical (not taking into account the amount of acid chloride taken for preparing the anilide.)

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N-Methyl-β-(β-naphthyl)-β-alanine

</div>

a) β-Naphthaldehyde (1.56 g), malonic acid (1.30 g), methylamine hydrochloride (1.01 g), anhydrous potassium acetate (1.50 g), and glacial acetic acid (5 ml) were heated on a boiling water bath for 8-9 hours. The originally homogeneous mixture evolved gas with formation of a crystalline precipitate. The thick crystalline mass obtained after cooling was extracted with dil. HCl (see synthesis of β-(β-naphthyl)-β-alanine). The hydrochloric acid filtrate was first concentrated on the water-bath and then extracted 4-5 times with ether and neutralized with a concentrated solution of sodium acetate. After a few hours, the precipitate that separated was filtered off, washed with water, and dried at 70-80°. 1.20 g of a substance of m.p. 187-188° (with decomposition) was obtained. After purifying for analysis by repeated crystallization, the substance melted at 195-195.5° (with decomposition).

N-Methyl-β-(β-naphthyl)-β-alanine crystallizes in prisms; it is easily soluble in mineral acids and in alkalis, and also, on boiling, in water and in acetone.

<div align="center">

Found %: N 5.82; 5.91

$C_{14}H_{15}O_2N$. Calculated %: N 6.11

</div>

The crystalline residue that remains on the filter after extracting the reaction mixture with hydrochloric acid was found to be pure β-(β-naphthyl)-acrylic acid, m.p. 207-208°. Yield 0.78 g (about 39% of theoretical).

b. Preparation from N-(β-naphthal)-methylamine. Dry N-(β-naphthal)-methyl-β-amine (1.69 g), malonic acid (1.04 g), and ethyl alcohol (5 ml) were boiled on the water-bath for 10 hours. Full dissolution occurred in the first 10 min., and a large amount of gas was evolved. After 30 min., a precipitate started to appear. After cooling, the reaction mass was treated in the way indicated above. Yield of crude N-methyl-β-(β-naphthyl)-β-alanine (m.p. 189-190°) C.68 g, i.e. 29.5% of theoretical. Yield of crude β-(β-naphthyl)-acrylic acid, 1.14 g, i.e. about 57.5% of theoretical.

SUMMARY

1. The method of preparing β-naphthaldehyde proposed by Sultanov, Rodionov, and Shemyakin, based on the oxidation of β-methylnaphthalene with selenium dioxide, has been improved by the use of naphthalene as solvent. The yield of aldehyde rose from 34 to 66-67% of theoretical.

2. N-(β-Naphthal)-methylamine and methyl β-(β-naphthyl)-acrylate are described for the first time.

3. The following have been synthesized: β-(β-naphthyl)-β-aminopropionic acid, its methyl ester, its amide, and its benzoyl and acetyl derivatives; the amide and anilide of N-acetyl-β-(β-naphthyl)-β-aminopropionic acid; and N-methyl-β-(β-naphthyl)-β-aminopropionic acid.

β-(β-Naphthyl)-β-aminopropionic acid has been prepared by the basic reaction of Rodionov and also by three variants of this method.

4. N-Methyl-β-(β-naphthyl)-β-aminopropionic acid has been prepared by two methods; one of them is new.

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SYNTHESIS OF 7-BENZ[a]ANTHRACENEMETHANEPHOSPHONIC AND 12-METHYL-7-BENZ[a]ANTHRACENEMETHANEPHOSPHONIC ACIDS[1])

B. A. Arbuzov and N. P. Grechkin

The carcinogenic hydrocarbons are oil-soluble, water-insoluble substances. Injection of carcinogenic substances in oil into the organism causes the undesirable formation of oleomas, i.e. tumors produced by the oil itself. For this reason attempts have been made to obtain substances having the skeleton of the carcinogenic hydrocarbons, but soluble in water. Thus there are the soluble complexes of carcinogenic hydrocarbons with desoxycholic acid [1], which were found to be of little use, owing to the fact that desoxycholic acid is a powerful hemolytic poison. Phenols derived from the carcinogenic hydrocarbons were found to be inactive [2]. There are also the compounds of the carcinogenic hydrocarbons with maleic anhydride, the salts of which are soluble in water [3], etc.

It seemed to us that, considering the important part played by organic derivatives of phosphorus in the organism, it would be interesting to prepare derivatives of actively carcinogenic substances containing the phosphonic group. Such acids or their salts might be soluble in water. With this in view we have examined the action of sodium diethyl phosphite on 7-benz[a]anthracenemethyl chloride. The resulting ester of the corresponding phosphonic acid (I) gave on hydrolysis the free phosphonic acid, whose sodium salt is soluble in water.
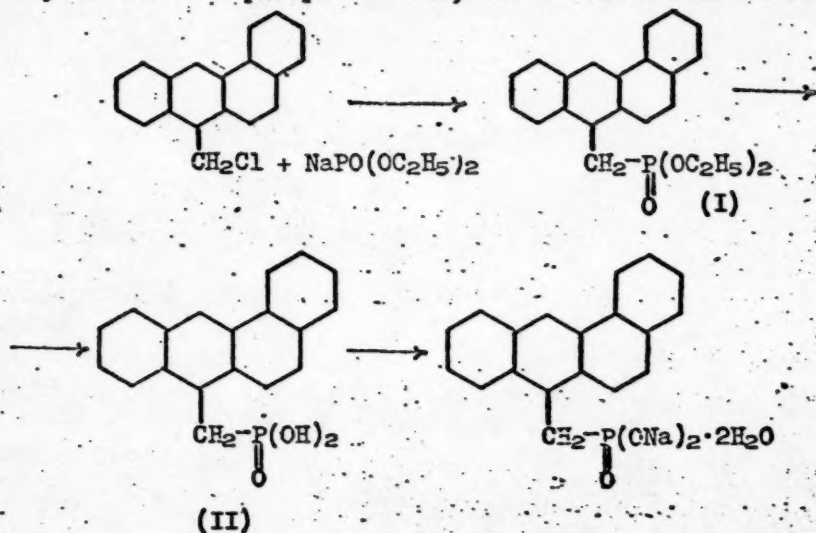
CH_2Cl + $NaPO(OC_2H_5)_2$

$CH_2-P(OC_2H_5)_2$
$\overset{\|}{O}$
(I)

$CH_2-P(OH)_2$
$\overset{\|}{O}$
(II)

$CH_2-P(ONa)_2 \cdot 2H_2O$
$\overset{\|}{O}$

From 12-methyl-7-benz[a]anthracenemethyl iodide, the corresponding phosphonic acid (III) was prepared through the ester in an analogous manner; its ammonium salt is of good solubility in water:
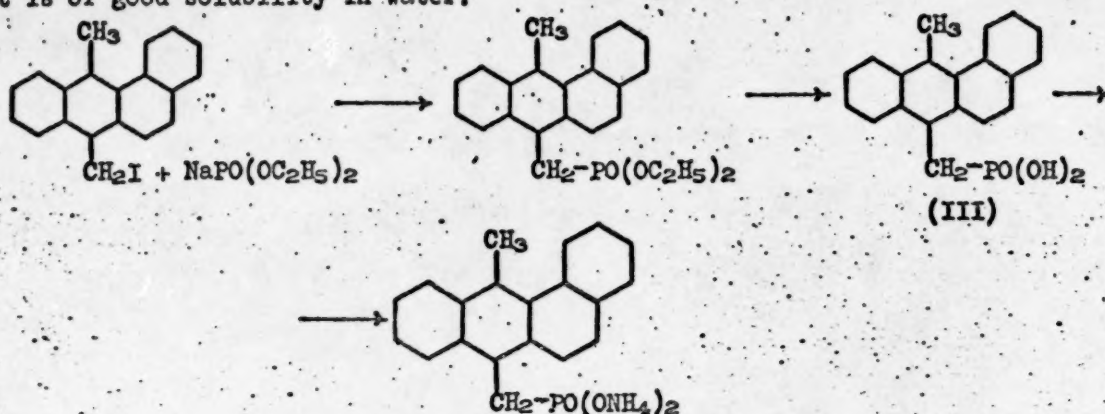
The substance III is a derivative of one of the most powerfully carcinogenic substances, 7,12-dimethylbenz[a]anthracene.

EXPERIMENTAL

Action of sodium diethyl phosphite on 7-benz[a]anthracenemethyl chloride

7-Benz[a]anthracenemethyl chloride (4 g) [4] is added to a benzene solution of the calculated amount of sodium diethyl phosphite at room temperature. The crystals of the former rapidly disappear, and the solution takes up a bright yellow color. The solution is boiled for an hour; the color of the solution becomes less intense, and a white precipitate forms on the walls of the flask. The solution is poured off, and the precipitate is washed with benzene by decantation. After the solution has stood for a short time, a small amount of crystalline material comes down; this is the unchanged benzanthracenemethyl chloride (m.p. 185-187°) — it gives no depression of m.p. in admixture with known substance. The benzene is distilled off in a vacuum, and a yellowish thick syrup remains behind. On hydrolyzing the syrup with conc. HCl under reflux for 30 min, 2.1 g of a solid substance is obtained. After reprecipitating twice (by acid from alkaline solution), 1.07 g of substance in the form of microcrystalline prisms is obtained; it is insoluble in water and in hydrochloric acid, but readily soluble in aqueous alkalis. The substance, dissolved in an aqueous solution of the calculated amount of caustic soda, is boiled with charcoal, filtered, and evaporated down to give 1.3 g of the sodium salt of 7-benz[a]-anthracenemethanephosphonic acid. Yield 23.6%, calculated on the original benzanthracenemethyl chloride.

Found %: P 7.72; 7.69
$C_{19}H_{12}O_3Na_2P \cdot 2H_2O$. Calculated %: P 7.73

After drying in a vacuum at 70° for 6 hr, the analysis was repeated:

Found %: P 8.50; 8.41
$C_{19}H_{12}O_3Na_2P$. Calculated %: P 8.46

Action of sodium diethyl phosphite on 12-methyl-7-benz[a]anthracenemethyl iodide

12-Methyl-7-benz[a]anthracenemethyl iodide (4.9 g) [5] is added in the cold

to a solution of 2.1 g of sodium diethyl phosphite in 50 ml of dry benzene. Reaction, with separation of sodium iodide, proceeds even in the cold. After boiling the solution for 15 min, the sodium iodide is filtered off (1.85 g = 95% of theoretical). The filtrate is a yellowish transparent liquid. The benzene is distilled off in a vacuum leaving a thick syrup. The latter is hydrolyzed with boiling conc. HCl under reflux for 24 hr, and a brownish solid (4 g) is obtained. After dissolving this in aqueous alkali and precipitating with hydrochloric acid, 2.1 g of a crystalline substance in the form of fine yellowish needles is obtained. This substance is dissolved by heating with excess of 25% ammonia. After evaporating the solution, 1.5 g of yellowish leaf-like crystals is obtained. Yield 30.6%, calculated on the original methylbenzanthracenemethyl iodide.

$$\text{Found } \%: \text{ P } 8.43; \ 8.56$$
$$C_{20}H_{23}ON_2P. \quad \text{Calculated } \%: \text{ P.8.38}$$

SUMMARY

The following phosphonic acids and their ethyl esters have been synthesized: 7-benz[a]anthracenemethanephosphonic acid and 12-methyl-7-benz[a]anthracenemethanephosphonic acid. These are derivatives of actively carcinogenic compounds.

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U.S.S.R. Academy of Sciences

LITERATURE

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INVESTIGATION OF ANTHRACENE DERIVATIVES

COMMUNICATION 10. THE RELATIVE ACTIVITIES OF THE MESO CARBON ATOM OF ANTHRACENE AND 9,10-DICHLOROANTHRACENE IN REACTIONS WITH OXIDIZING AGENTS

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One of us [1,2] has already shown that in the preparation of anthraquinone by oxidizing anthracene in aqueous suspension with chlorine the reaction finally slows down considerably when the main component of the mixture, apart from anthraquinone, becomes 9,10-dichloroanthracene, which is a by-product in the reaction. As the concentration of chlorine in the solution was maintained constant, we considered that the slowing down was to be explained by the greater reluctance of 9,10-dichloroanthracene to undergo oxidation, as compared with anthracene itself. In this connection, we have now determined the reaction rates for the oxidation of anthracene and of 9,10-dichloroanthracene by chlorine water and have shown that reaction with anthracene is many times more rapid than with 9,10-dichloroanthracene. At the same time we have shown that also with other oxidizing agents, e.g. $K_2Cr_2O_7 + H_2SO_4$ and $KMnO_4 + KOHaq$, reaction with anthracene is considerably more rapid than with 9,10-dichloroanthracene. The course of the reaction was followed by determining the concentration of oxidizing agent in solution at definite intervals of time. The relative rates of oxidation of anthracene and of 9,10-dichloroanthracene and the relative activities of the meso-carbon atoms of these compounds in these reactions were estimated according to the consumption of oxidizing agent.

EXPERIMENTAL

Starting materials. Anthracene, chemically pure, m.p. 216°, was prepared by recrystallizing 93-94% anthracene twice from benzene, distilling, and then again crystallizing from toluene. 9,10-Dichloroanthracene was prepared by the method already described by one of us [3]. After three crystallizations from benzene, the first in conjunction with activated wood charcoal, 9,10-dichloroanthracene was obtained in the form of pale-yellow needles, m.p. 212.4°. Further crystallization did not affect the melting point.

In view of the fact that the reactions under investigation are carried out under heterogeneous conditions, it was necessary, in order to obtain comparative results, to pay particular attention to regularity of particle size, standard pasting procedure, and standard conditions for stirring during reaction. Only by careful observation of standard conditions in these operations was it possible to obtain results agreeing within 2-3% in duplicate experiments.

Anthracene and 9,10-dichloroanthracene were carefully ground, first in the dry state, and then as an aqueous paste, which was rubbed through silk gauze having 64 mesh per cm. The pastes obtained were pressed off on a filter, dried, and again ground. For the preparation of chlorine water, chlorine from a cylinder was used. Chemically pure dichromate and permanganate were used.

I. Oxidation with Chlorine Water

Experimental Procedure. The determination of the rate of the reaction of

anthracene (9,10-dichloroanthracene) with chlorine water was carried out in a flask of about 400 ml capacity with a ground-in stopper; the flask was fixed by the aid of screw clamps in a vertical position in a jacket with a rubber seal. The jacket was attached to a shaker, which gave 70-75 shakes per min. Depending on the conditions of the experiment, either water or a cooling mixture was passed through the jacket; the temperature of the cooling agent was measured as the latter went in and came out of the jacket. The flask was checked for leaks by means of blank experiments in which chlorine water only was shaken for some hours and its concentration determined. The chlorine water was prepared by saturating freshly distilled water with chlorine from a cylinder, and it was kept in a vessel of dark-colored glass with a ground-in stopper. The required concentration of chlorine was obtained by subsequently diluting the solution with distilled water, and before each experiment the concentration was checked by iodometric titration. The required amount of chlorine water was taken with the aid of a special, previously calibrated pipet, similar in construction to Yakovkin's pipet [4], with a three-way tap and bulb, designed to remove the top layer of the chlorine water that is drawn up.

The weighed amount of anthracene (9,10-dichloroanthracene), ground up in the manner already described, is pasted up with 0.5 ml of water in a thin glass test-tube and introduced into the reaction flask, into which, after allowing about half an hour for the temperature of the experiment to be reached, a definite volume of chlorine water is introduced by the aid of the pipet. The reaction is considered to start at the moment when the anthracene (9,10-dichloroanthracene) is introduced: on shaking, the test tube is broken, and the substance under investigation is uniformly distributed in the chlorine water.

After a definite interval of time the shaker is stopped and the course of the reaction is interrupted by adding an excess of 10% KI; the iodine liberated is titrated with thiosulfate. In some of the experiments the acidity of the solution was determined alkalimetrically (after the iodometric titration) in presence of phenolphthalein. For each period of time, at least two experiments were carried out for each temperature. Most of the experiments were carried out with an excess of anthracene over that calculated from the equation for oxidation to anthraquinone:

$$C_6H_4 \begin{smallmatrix} CH \\ \\ CH \end{smallmatrix} C_6H_4 + 3Cl_2 + 2H_2O = C_6H_4 \begin{smallmatrix} CO \\ \\ CO \end{smallmatrix} C_6H_4 + 6HCl. \qquad (1)$$
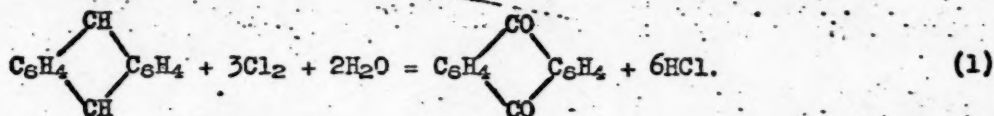
According to this equation, 33.69 ml of 0.1 N chlorine is required for 0.1 g of anthracene. The amount of chlorine consumed in the oxidation was determined from the difference between the amount of chlorine taken for the experiment and the amount remaining after the reaction, working in ml of 0.1 N solution and recalculating as % of the amount of chlorine required for complete oxidation. The results of experiments in which the effect of the chlorine concentration and the temperature on the rate of oxidation of anthracene is studied are given in Tables 1, 2, 3, 4, and 5 and in Fig. 1. The results of experiments on the oxidation of 9,10-dichloroanthracene by chlorine water are given in Table 6 and Fig. 1.

The following are the signs used in the tables and in the text: t is the time from the start of the experiment (min); A_0 is the volume of 0.1 N chlorine water at the start of the experiment (ml); $A_0 - x$ is the volume of 0.1 N chlorine water remaining after the oxidation (ml); x is the volume of 0.1 N chlorine water consumed in the oxidation (ml); k_1 is the value of the first-

order constant calculated from the equation:

$$k_1 = \frac{2.303}{t} \log \frac{A_0}{A_0 - x} \qquad\qquad (2)$$

and k_2 is the value of the first-order constant calculated from the equation:

$$k_2 = \frac{1}{t} \left[2.303 \, A_0 \log \frac{A_0}{A_0 - x} - x \right]. \qquad\qquad (3)$$
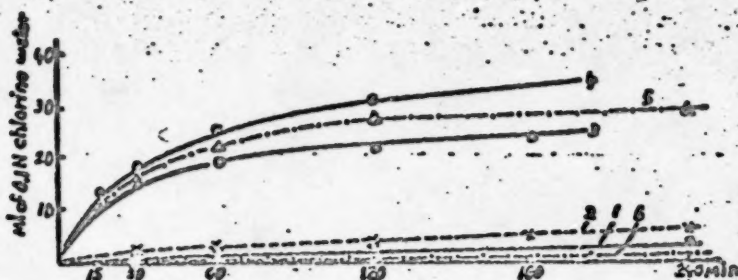
Fig. 1. Oxidation of anthracene (curves 1-5) and of 9,10-dichloroanthracene (curve 6) by chlorine water: 1) 50.07 ml 0.01 N chlorine water, t 2-3°; 2) 50.07 ml 0.05 N chlorine water, t 2-3°; 3) 50.07 ml 0.05 N chlorine water, t 15-16°; 4) 99.31 ml 0.05 N chlorine water, t 15-16°; 5) 99.31 ml 0.05 N chlorine water, t 15-16° in presence of hydrochloric acid; 6) 50.07 ml 0.05 N chlorine water, t 20-21°

In spite of the complex nature of the processes occurring in the heterogenous system investigated, we have attempted to give our measurements a kinetic treatment, and we have obtained comparatively satisfactory results by treating the reaction as being formally of the first order with respect to active chlorine. For the purpose of the kinetic investigation of the oxidation of anthracene, we took into account the courses of the chemical reactions, but not the processes occurring at the bounding surfaces and also not the diffusion processes, although, as the experiments show, the latter play an essential role.

From an examination of the experimental results in the tables and in Fig. 1, the following preliminary conclusions can be made:

1) The reaction rate increases approximately proportional to the analytically determined concentration of active chlorine (Tables 1 and 2).

2) The reaction rate is reduced by the hydrochloric acid that is formed or is introduced prior to the reaction (Fig. 1, curves 4 and 5; Tables 1-5).

3) The reaction rate for the oxidation of anthracene is considerably greater than that for the oxidation of 9,10-dichloroanthracene (Fig. 1, curves 3 and 6; Tables 3 and 6).

In order to derive a kinetic equation on the basis of this information we must take into consideration that the rate of change of the concentration of oxidizing agent at any given moment is proportional to the analytically determined concentration of active chlorine and inversely proportional to the con-

centration of hydrochloric acid:

$$-\frac{d[Cl_2]}{dt} = k_2' \frac{[Cl_2]}{[HCl]} .$$

Introducing our symbols and converting to a form that is suitable for integration:

$$-\frac{d[A_0 - x]}{dt} = k_2' \frac{[A_0 - x]}{[x]} \quad \text{and} \quad \frac{xd[A_0 - x]}{A_0 - x} = -k_2 dt.$$

After integration this equation assumes the form:

$$k_2 = \frac{1}{t}\left[A_0 \ln \frac{A_0}{A_0 - x} - x\right] . \tag{4}$$

TABLE 1

Expt. No.	t, min.	A_0, ml	$A_0 - x$, ml	x, ml	k_1	k_2	Percent of amount theoretically necessary for oxidation
1	15	5.95	5.65	0.30	0.0034	0.00054	0.89
2	30	5.96	5.53	0.43	0.0025	0.00054	1.27
3	60	5.98	5.36	0.62	0.0018	0.00057	1.84
4	120	6.00	5.10	0.90	0.0010	0.00062	2.67
					Mean	0.00056	

Amount of anthracene taken, 0.1 g; 50.07 ml of chlorine water was taken for each experiment; temperature of experiment 2-3°.

TABLE 2

Expt. No.	t, min.	A_0, ml	$A_0 - x$, ml	x, ml	k_1	k_2	Percent of amount theoretically necessary for oxidation
1	30	26.19	24.41	1.78	0.0023	0.0021	5.27
2	60	27.09	24.55	2.54	0.0016	0.0021	7.53
3	120	25.78	22.54	3.24	0.0011	0.0019	9.40
4	180	25.88	21.72	4.16	0.0009	0.0021	12.28
					Mean	0.0021	

Amount of anthracene taken, 0.1 g; 50.07 ml of chlorine water was taken for each experiment; temperature of experiment 2-3°.

From this equation we calculated the rate constants for the reaction. These are given in Tables 1, 2, 3, 4, and 5. It must be pointed out that the calculated reaction rate constants are conventional only, but are of significance for comparative purposes.

If, however, the rate constant is calculated from the equation

$$-\frac{d[Cl_2]}{dt} = k_1[Cl_2] ,$$ then a constant is obtained that falls rapidly, as will be

seen from the tables. For convenience of discussion, the results obtained are brought together in Table 7.

As will be seen from Series 1 and 2, the rate constant is approximately proportional to the concentration of active chlorine. On the other hand, increase in the amount of chlorine at a given temperature and for a given concentration of active chlorine may even cause a fall in the constant for the series (Series 3 and 4), which is probably to be explained by the increase in the volume of the liquid phase. A 1° rise in temperature results in a ten-fold increase in the rate constant. The hydrochloric acid formed reduces the reaction rate (Tables 1-4), and the prior introduction of hydrochloric acid to the extent of about 0.02 mole causes a fall in the constant by about 10% (Series 4 and 5).

TABLE 3

Expt. No.	t, min.	A_0, ml	$A_0 - x$, ml	x, ml	k_1	k_2	Percent of amount theoretically necessary for oxidation
1	15	25.93	14.52	11.41	0.03866	0.2420	33.8
2	30	25.93	10.82	15.11	0.02915	0.2520	44.8
3	60	25.89	6.79	19.10	0.02231	0.2594	55.4
4	120	25.95	3.86	22.09	0.01588	0.2280	65.5
					Mean	0.2452	

Amount of anthracene taken, 0.1 g; 50.07 ml of chlorine water was taken for each experiment; temperature of experiment 15-16°.

TABLE 4

Expt. No.	t, min.	A_0, ml	$A_0 - x$, ml	x, ml	k_1	k_2	Percent of amount theoretically necessary for oxidation
1	15	48.82	35.10	13.72	0.02200	0.1592	40.7
2	30	48.36	30.40	17.96	0.01548	0.1494	53.3
3	60	51.44	26.66	24.78	0.01095	0.1505	73.5
4	120	49.24	18.98	30.26	0.00790	0.1392	89.8
5	240	48.96	17.55	31.41	0.00430	0.0784[1]	93.2
					Mean	0.1495	

[1] Rejected when calculating mean.
Amount of anthracene taken, 0.1 g; 99.31 ml of chlorine water was taken for each experiment; temperature of experiment 15-16°.

When the percentage conversion of the anthracene reaches about 90, a sharp fall in the value of the constant is observed; this occurs in Experiment 5, Table 4 and in Experiment 4, Table 5. This fall in the constant is to be explained by the accumulation in the reaction products of 9,10-dichloroanthracene; the rate of the oxidation of 9,10-dichloroanthracene is many times less than that of anthracene under the same conditions of temperature and chlorine concentration (Fig. 1, curves 3 and 6; Tables 3 and 6).

TABLE 5

Expt. No.	t, min.	A_0, ml	$A_0 - x$, ml	x, ml	k_1	k_2	Percent of amount theoretically necessary for oxidation
.1	30	45.65	29.04	16.61	–	0.1340	49.30
2	60	46.18	23.42	22.76	–	0.1430	67.54
3	120	45.48	18.05	28.43	–	0.1300	84.36
4	240	46.16	29.94	29.94	–	0.0740[1]	88.84
					Mean	0.1356	

[1] Rejected when calculating mean.

Amount of anthracene taken, 0.1 g; 99.31 ml of chlorine water was taken for each experiment. The experiments were carried out in presence of hydrochloric acid, concentration 0.02232 mole per liter; the temperature of the experiment was 15-16°.

TABLE 6

Expt. No.	t, min.	A_0, ml	$A_0 - x$, ml	x, ml	k_1	k_2	Percent of amount theoretically necessary for oxidation
1	60	30.38	30.26	0.12	–	–	1.48
2	120	30.53	30.30	0.22	–	–	2.71
3	180	30.82	30.34	0.48	–	–	5.92
4	240	29.92	29.36	0.56	–	–	7.08

Amount of 9,10-dichloroanthracene taken, 0.1 g: 50.07 ml of chlorine water was taken for each experiment; temperature of experiment, 20-21°.

TABLE 7

Expt. Series No.	Temp. (°C)	Moles chlorine per mole of anthracene	Concentration of chlorine water	k_2	Ratio of constants	
1	2-3	1.07	0.012	0.00056	$k_2^2 : k_2^1$	=3.75[1]
2	2-3	4.67	0.0524	0.0021		
3	15-16	4.62	0.0518	0.2452	$k_2^3 : k_2^1$	=1.17
4	15-16	8.91	0.0504	0.1495	$k_2^3 : k_2^4$	=1.64
5	15-16	8.91	0.0504	0.1356	$k_2^4 : k_2^5$	=1.1

[1] The superscript numbers indicate the number of the series.

The Products Obtained by the Action of Chlorine on Anthracene in Aqueous Suspension

When halogens react with anthracene and other organic compounds in aqueous suspension, or in suspension in aqueous solutions of alcohol, acetone, or acetic acid, mainly oxidative processes occur.

Meyer [5] and Zahn [6], by the action of chlorine or bromine on anthracene suspended in aqueous solutions of alcohol or acetic acid at 25°, obtained oxanthranol, which was converted into anthraquinone by the prolonged action of chlorine; at a high temperature, the main reaction was the oxidation of anthracene to anthraquinone. They observed also the formation of 9,10-dichloroanthracene as a by-product. Plazek [7], by the action of chlorine on anthracene in methanol or ethanol, obtained anthraquinone in very good yield and in a high state of purity. Charrier and Grippa [8], by the action of hypochlorous acid on anthracene in aqueous suspension, obtained a product that they took to be a mixture of 9-hydroxy-10-chloroanthracene and 9-hydroxy-10-chlorodihydroanthracene. The mixture of these products was converted by boiling with alcohol into bis(9-hydroxy-10-anthryl) ether. Price and Weaver [9], by the action of bromine on anthracene in dry acetone, obtained a good yield of 9,10-dibromoanthracene (m.p. 221°). When the acetone employed was not carefully dried, the products were always 9-bromoanthrone (m.p. 142-144°) and anthraquinone (m.p. 280-282°), and when the water content of the acetone was high, anthraquinone was the sole product.

We have investigated the products obtained by the action of 1200 ml of a 0.05 N aqueous solution of chlorine on 2.5 g of anthracene at 15-16° for 60 hours and have isolated the following products:

1. The reaction product was treated several times with a hot 4-5% solution of caustic soda until the filtrate ceased to have a red color. When the color became brownish yellow, the caustic soda solution was diluted to 0.5%, and extraction was continued until a colorless filtrate was obtained. On acidifying the red filtrate with dil. HCl or H_2SO_4, a brownish-yellow substance was precipitated, and from this, by crystallization from glacial acetic acid, two substances were isolated.

a) The first (about 1%) crystallized out after cooling the acetic acid solution and was obtained, after recrystallization, in the form of yellow needles, m.p. higher than 300°. The substance does not contain chlorine and yields anthraquinone, m.p. 285°, on oxidation with chromic acid in acetic acid. It gives a bluish-red solution in conc. H_2SO_4. Its structure was not established.

<center>Found %: C 87.1; H 4.1</center>

b) The second substance (about 7%), which was isolated by diluting the filtrate, was obtained, after crystallizing twice from alcohol, in the form of light-yellow crystals, melting over the range 161-170°; it was identified as a mixture of 9,10-dihydroxyanthracene and oxanthranol. The substance does not contain chlorine, dissolves in a 3-4% solution of caustic soda to give a red solution, and rapidly oxidizes to anthraquinone. It gives a wine-red solution in sulfuric acid. A mixed melting point with synthetic 9,10-dihydroxyanthracene shows no depression.

By acidification of the brownish-yellow filtrate, a substance was isolated, which was identified with anthranol (about 3%). After crystallization from alcohol, it was obtained in the form of brownish-yellow needles, m.p. 161-167°. The substance does not contain chlorine, gives a brownish-yellow solution in alkali, and is oxidized by chromic acid to anthraquinone. It gives a greenish-

yellow solution in conc. H_2SO_4, which becomes bluish-red on the addition of nitric acid. It shows a blue fluorescence in alcoholic solution. Positive results are obtained in the characteristic reaction for anthranol [10]: by the action of fuming nitric acid a substance is formed that, after precipitation with water, may be dissolved in alcohol to give an orange solution; this solution becomes violet on addition of alkali.

2. The residue after the treatment with aqueous alkali was treated repeatedly with a solution containing, per 100 ml, 8 g of sodium hydrosulfite and 8 g of caustic soda at a temperature of 60-80°. After oxidation of the red filtrate by means of the oxygen of the air, anthraquinone (61-62%), m.p. 285-286°, was precipitated.

3. The residue after the separation of alkali-soluble compounds and of anthraquinone comprised about 25% of the anthracene taken and consisted of anthracene and 9,10-dichloroanthracene, the amounts of which were determined in the following way: the material was recrystallized from a very small amount of glacial acetic acid, and the product (0.3574 g, m.p. 160-170°) was dissolved in 10 ml of glacial acetic acid and heated with a solution of 5.4 g of CrO_3 in 8 ml of 50% acetic acid for 20 min; the solution was then poured into 100 ml of ice-water, and the precipitated anthraquinone was filtered off, washed, and dried. Weight of anthraquinone, m.p. 286°, 0.3630 g. Hence we find: anthracene 53.2%, and 9,10-dichloroanthracene 46.8%

Found %: Cl 13.41 (Carius)
Calculated %: Cl 13.7 (according to the composition found).

After several crystallizations of the remaining mixture, anthracene, m.p. 214-215°, and 9,10-dichloroanthracene, m.p. 208-209°, were isolated. Consequently, by the action of chlorine water on anthracene at 15-16° for 50-60 hours, a mixture of products were obtained, among which the following were found:

Anthraquinone 61-62%
Anthrahydroquinone and oxanthranol 7%
Anthranol 3%
9,10-Dichloroanthracene ~ 12%
Anthracene (unreacted) 13%
Substance, m.p. > 300° ~ 1%.

Some observations on the mechanism of the reaction. As is well known, anthracene is peculiar in its chemical behavior in that the initial reactions generally consist in addition reactions of various species to the meso carbons of anthracene, and anthracene stands more closely in this respect to the olefins than to the aromatic hydrocarbons. Thus, when halogenated, nitrated, hydrogenated, or metallized, and in diene syntheses and in the formation of photo-oxides, anthracene forms, in the first stage, stable addition products, whereas no such addition products have been isolated in the analogous reactions of benzene and naphthalene. We consider that in the oxidation of anthracene the first step in the reaction is the formation of addition products of anthracene, although some of these (e.g. 9,10-dihydroxydihydroanthracene) have not been isolated in the free condition.

We consider that when anthracene reacts with chlorine water two simultaneous oxidation processes occur: in one of these chlorine takes part, and in the other — hypochlorous acid. This idea is in agreement with Shilov's views [11] on the process of chlorine bleaching, which he has developed from the kinetics of the addition of hypochlorous acid at a double bond [12]. According to

Shilov, the reaction of chlorine water with a reducing agent is to be treated as a complex process, comprising oxidation, addition, and chlorination reactions. Let us consider the two processes.

1. One of us [2] has previously suggested that the oxidizing agent in chlorine water is the molecule of chlorine at the moment of its reaction with water. We have assumed a mechanism for the oxidation of anthracene by chlorine water in which chlorine molecules that have been polarized by the electric field of water molecules take part:

$$\overset{\oplus}{\underset{\oplus}{H}}O^{\ominus} + Cl_2 \longrightarrow H\text{---}O\text{---}H\ldots\ldots \underset{+\delta}{Cl} \longrightarrow \underset{-\delta}{Cl} \qquad (6)$$
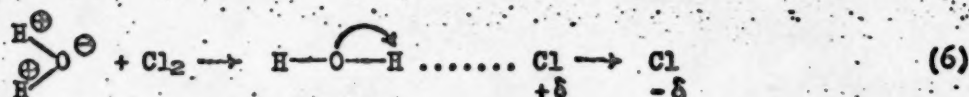
Thus we assume that in the equilibrium existing in chlorine water we have, as well as chlorine molecules, water, hypochlorous acid, hydrogen ions, and chlorine, also chlorine molecules that are polarized in the electric field of water molecules, in accordance with the following equilibrium equation:

$$Cl_2 + H_2O \rightleftharpoons H\text{---}O\text{---}H\ldots\ldots \underset{+\delta}{Cl} \longrightarrow \underset{-\delta}{Cl} \rightleftharpoons HOCl + H^+ + Cl' \qquad (7)$$
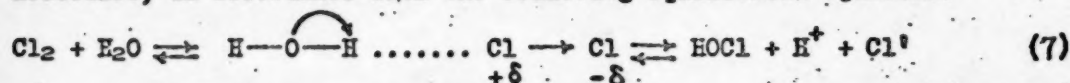
The mechanism of the oxidation of anthracene by chlorine water with the participation of the molecules:

$$H\text{---}O\text{---}H\ldots\ldots \underset{+\delta}{Cl} \longrightarrow \underset{-\delta}{Cl}$$
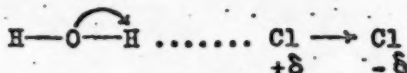
has been indicated previously by one of the authors [2].

The delaying effect of hydrochloric acid is to be explained by the displacement of the equilibrium of Equation 7 from right to left; the compound of the activated molecules, $H - O - H\ldots\ldots\underset{+\delta}{Cl} \longrightarrow \underset{-\delta}{Cl}$
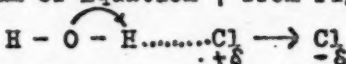
is decomposed with formation of non-hydrated chlorine.

2. The oxidative process that is to be attributed to hypochlorous acid, which is formed by the hydrolysis of chlorine in accordance with Equation 7, proceeds by the following reaction:

$$C_6H_4 \overset{\overset{H}{\underset{|}{C}}}{\underset{\underset{|}{C}}{}} C_6H_4 + 3HOCl = C_6H_4 \overset{CO}{\underset{CO}{}} C_6H_4 + 3HCl + H_2O. \qquad (8)$$
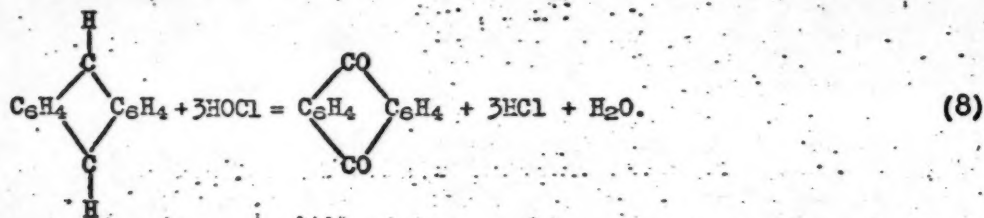
The hydrochloric acid that is formed in accordance with Equation 8 will clearly displace the equilibrium of Equation 7 from right to left, so that the concentration of hypochlorous acid will fall and reaction 8 will be slowed down. The equilibrium reaction 7 is the slowest of the reactions occurring and determines the order of the reaction.

The mechanisms of the reactions that explain the formation of the products indicated above may be formulated in the following way. As the meso carbons of anthracene are nucleophilic centers, they will be subject, above all, to the action of the halogen $\left(\underset{+\delta}{Cl}\right)$ which is poor in electrons, of the hypochlorous acid,

with formation of the hypothetical cation (I), which can react with water according to (a) or (b), or can react with any anion in the solution.

The course of the successive reactions of anthracene with hypochlorous acid are shown in the diagrammatic scheme.

We have not succeeded in isolating, as reaction products, 9-chloroanthracene (II) and 9-chloroanthrone (III), but they are probably formed.

This interpretation of the oxidation of anthracene by means of chlorine water is in accord with the reactions of anthracene with bromine in aqueous acetone [9] and of olefins with hypochlorous acid [13].

II. Oxidation with Dichromate and Permanganate
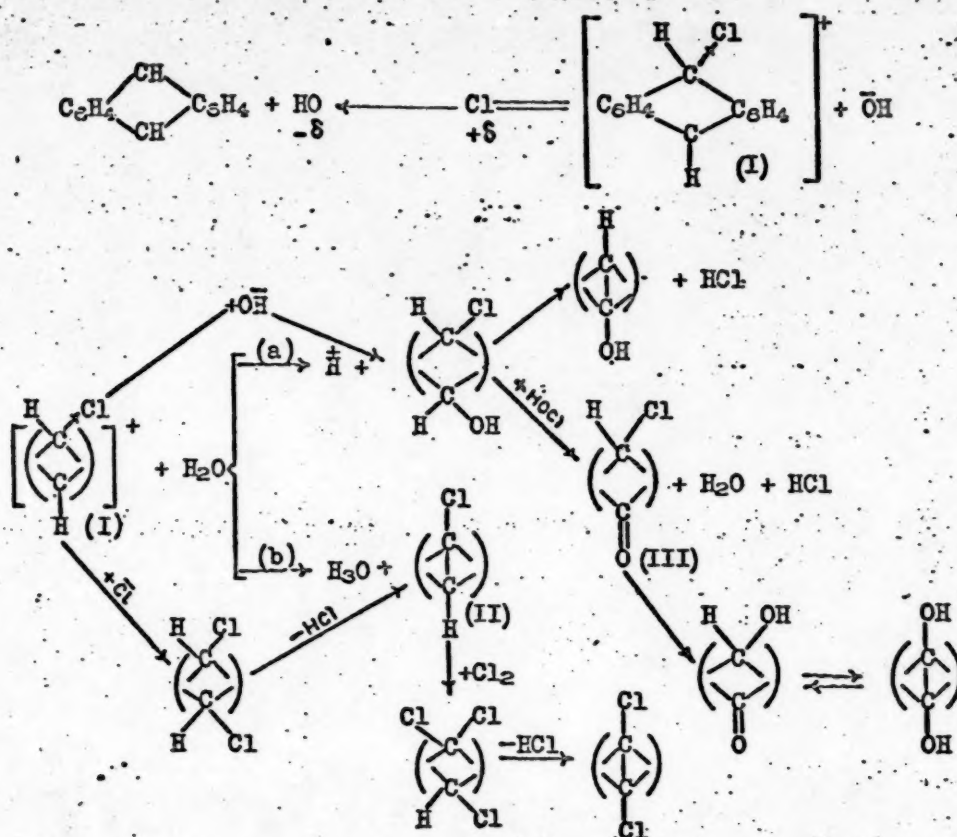
Experimental Procedure. The determination of the rate of reaction of anthracene (9,10-dichloroanthracene) with dichromate or permanganate was carried out in a three-necked round-bottomed flask of 250 ml capacity with a reflux condenser. Through the condenser there passed a thermometer, a stirrer, and also a T-tube, in the side arm of which a glass rod was fixed by means of rubber tubing so that it held back a thin-walled test-tube containing the weighed amount of anthracene (9,10-dichloroanthracene). When the test-tube containing the sample had been placed in position on the rod, the upper end of the T-piece was closed with a stopper. The speed of stirring was kept constant (85-90 rev/min) in all experiments. Oxidizing agent, as a 0.1 N solution, was taken in known excess

over the amount calculated according to the equation for the oxidation of anthracene (9,10-dichloroanthracene) to anthraquinone.

The test-tube containing the weighed amount of anthracene (or 9,10-dichloroanthracene), which had been mixed into a fine suspension with 4 ml of a 1% solution of sulfuric acid or with 4 ml of a 17.5% solution of caustic potash, was lowered, by withdrawing the rod, into 100 ml of the 0.1 N solution of the oxidizing agent, heated to boiling point (on a glycerol bath). The reaction was considered to start from that moment. After a definite interval of time, the solution was cooled rapidly and filtered. The amount of oxidizing agent remaining after the reaction was determined by iodometric titration.

The results of the experiments are given in Tables 8 and 9 and in Fig. 2.

It will be seen from Tables 8 and 9 and from Fig. 2 that, in the first place, the rate of oxidation of anthracene, both in acid and in alkaline medium, is notably higher than that of 9,10-dichloroanthracene and, in the second place, that the rate of oxidation of 9,10-dichloroanthracene is higher in alkaline medium than in acid medium. The latter fact leads us to assume that in the general

TABLE 8
Oxidation by potassium dichromate in presence of sulfuric acid

Amount taken (g)	Time from start of expt. (min)	Amount of oxidizing agent taken (ml 0.1 N)	Amount of oxidizing agent used (ml 0.1 N)	Theor. required amt. of oxidizing agent (ml 0.1 N)	Amt. of oxidizing agent used as % of theor. reqd. amount	Remarks
			Anthracene			
0.2981	30	101.1	14.70	102.0	14.31	In all cases, 2 or
0.2953	60	101.1	22.59	101.0	22.3	3 experiments were
0.2961	120	101.1	46.70	101.3	46.10	carried out for
0.2909	240	101.1	67.12	99.54	67.45	each period of time
			9,10-Dichloroanthracene			
0.4383	60	101.1	0.12	36.04	0.34	
0.4403	120	101.1	0.57	36.65	1.58	
0.4292	240	101.1	2.64	36.33	7.26	
0.4176	360	101.1	5.37	34.42	15.60	

chain of reactions from 9,10-dichloroanthracene to anthraquinone the oxidation reaction is preceded by the replacement of the halogens by hydroxyls with formation of 9,10-dihydroxyanthracene. 9,10-Dihydroxyanthracene appears to be an intermediate product also in the oxidation of anthracene. These considerations and also the fact that in oxidation reactions the meso carbon atoms of anthracene in taking up the configuration of anthraquinone lose three electrons, whereas 9,10-dichloroanthracene loses only one electron in the same process, lead one to assume the following scheme of changes:
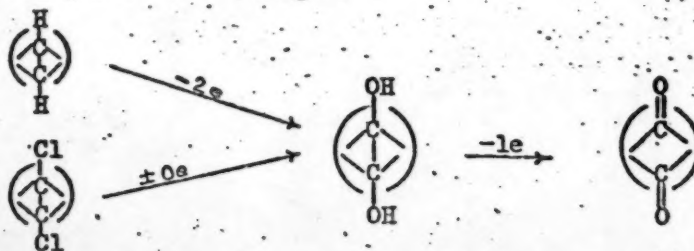
TABLE 9

Oxidation by potassium permanganate in alkaline solution

Amount taken (g)	Time from start of expt. (min)	Amount of oxidizing agent taken (ml 0.1 N)	Amount of oxidizing agent used (ml 0.1 N)	Theor. required amt of oxidizing agent (ml 0.1 N)	Amt. of oxidizing agent used as % of theor. reqd. amount	Remarks
Anthracene						
0.1484	15	99.49	41.62	84.21	49.42	In all cases, 2 or
0.1493	30	99.49	57.93	84.72	68.38	3 experiments were
0.1485	45	99.49	75.85	84.27	90.01	carried out for
0.1486	60	99.49	85.10	84.34	100.8	each period of time
9,10-Dichloroanthracene						
0.6186	30	99.49	14.33	84.34	17.0	
0.6186	60	99.49	27.76	83.65	33.18	
0.6158	120	99.49	52.2	83.95	62.18	
0.6186	240	99.49	76.64	84.34	90.87	
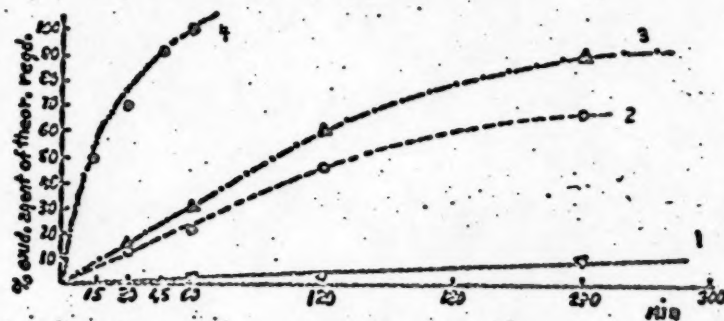
Fig. 2. Oxidation of anthracene (curves 2,4) and of 9,10-dichloroanthracene (1,3): 1) $K_2Cr_2O_7$ + H_2SO_4aq (9,10-dichloroanthracene); 2) $K_2Cr_2O_7$ + H_2SO_4aq (anthracene); 3) $KMnO_4$ + KOHaq (9,10-dichloroanthracene); 4) $KMnO_4$ + KOHaq (anthracene)

SUMMARY

1. Measurements have been made of the rate of the reaction between anthracene (9,10-dichloroanthracene) in aqueous suspension and chlorine at 2-3° and at 15-16°, using chlorine concentrations of 0.01 N and 0.05 N. The oxidation by chlorine of anthracene in aqueous suspension proceeds as a first-order reaction with respect to active chlorine. The reaction rate increases with increase in the concentration of active chlorine and is reduced by the hydrochloric acid that is formed; it is expressed by the equation:

$$-\frac{d[Cl_2]}{dt} = k'_2 \frac{[Cl_2]}{[HCl]}$$

2. It has been shown that the rate of oxidation of anthracene by chlorine water falls sharply towards the end owing to the formation of 9,10-dichloroanthracene, for the rate of the oxidation of the latter is many times less than the rate of the anthracene reaction.

3. The products of the oxidation of anthracene by aqueous chlorine at 15-16° for 60 hr have been isolated and identified. They are: anthraquinone (62%), 9,10-dihydroxyanthracene and oxanthranol (7%), 9-hydroxyanthracene (3%), 9,10-dichloroanthracene (12%), and unchanged anthracene (13%).

4. The mechanism of the oxidation of anthracene by aqueous chlorine has been indicated.

5. Measurements have been made of the rate of oxidation of anthracene and of 9,10-dichloroanthracene by the oxidizing agents: $K_2Cr_2O_7 + H_2SO_4$aq and $KMnO_4 + KOH$aq.

It has been shown: 1) that the rate of oxidation of anthracene, both in acid and in alkaline solution, is many times higher than the rate of oxidation of 9,10-dichloroanthracene, and 2) that the rate of oxidation in alkaline medium is 4 to 5 times higher than in acid medium in the case of anthracene and is 60 to 80 times higher in the case of 9,10-dichloroanthracene.

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REACTIONS OF METHYLCYCLOHEXANE AND TOLUENE IN CONTACT
WITH ALUMINUM CHLORIDE

N. I. Shuykin and L. M. Feofanova

The isomerization of cycloalkanes, particularly the conversion of one ring into another, under the action of anhydrous aluminum bromide or chloride has been studied over a long period by Zelinsky and his coworkers [1], and also by some foreign authors [2]. A number of investigators have noted that reactions of another type occur at the same time; these consist in the transference of methyl side groups from one ring to another. Thus there are indications that the isomerization of cyclohexane into methylcyclopentane in presence of aluminum chloride:
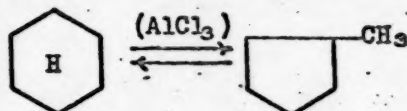
which has been studied over a range of temperatures and pressures, is accompanied by the formation of a certain amount of 1,3-dimethylcyclohexane [3].

An analogous process consisting in the redistribution of methyl groups among molecules under the action of aluminum chloride is observed also in the reactions of xylene [4]. One of us has shown [5] that when aluminum chloride acts upon an equimolecular mixture of xylene and benzene at 250-300° a redistribution of methyl groups occurs with formation of toluene:

$$C_6H_4(CH_3)_2 + C_6H_6 \rightarrow 2C_6H_5CH_3.$$
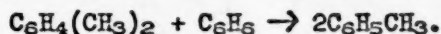
In this connection it appeared to be of interest to determine the behavior of the simplest homolog of benzene, toluene, and also of methylcyclohexane, in contact with anhydrous aluminium chloride at a comparatively low temperature (80°), i.e. under conditions that preclude, on the one hand, the occurrence of cracking and, on the other hand, the formation of more complex polycyclic systems. In the investigation of the behavior of methylcyclohexane under these mild conditions it was of interest to determine whether in addition to dimethylcyclopentanes — the possible products of the isomerization of methylcyclohexane with shrinkage of the ring — dimethylcyclohexanes are formed.

In the experiments with toluene, the determination of the possibility of the formation of benzene and xylene under the selected conditions was of special interest. The main experiments were carried out with fairly large amounts (400 g of each) of methylcyclohexane and toluene, and it was therefore possible, by the aid of precise rectification, to identify all the products of the possible reactions, even when they were formed in small amount. Investigation of the reaction products showed that the main reaction of methylcyclohexane in presence of aluminum chloride at 80° is isomerization with shrinkage of the ring into dimethylcyclopentanes (mixture of 1,3- and 1,2 isomers):
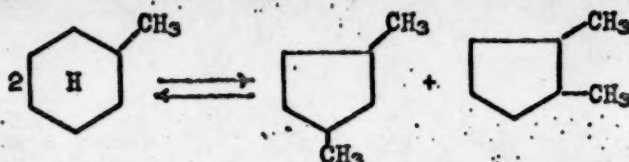
This equilibrium stands very much on the left side under our conditions, for only about 2-5%, depending on the time of contact with $AlCl_3$, of the methyl-cyclohexane taken is converted into dimethylcyclopentanes. Transalkylation, i.e. the redistribution of methyl groups, occurs to an insignificant extent: only very small amounts of cyclohexane and dimethylcyclohexane could be found among the reaction products. When toluene is brought into contact with aluminum chloride under analogous conditions, redistribution of methyl groups is more in evidence. Among the reaction products there were found, in addition to the main mass of unchanged toluene, benzene and all the isomeric xylenes, with a predominance of m-xylene, in appreciable amounts:

$$2C_6H_5CH_3 \underset{}{\overset{AlCl_3}{\rightleftarrows}} C_6H_6 + C_6H_4 \cdot (CH_3)_2.$$
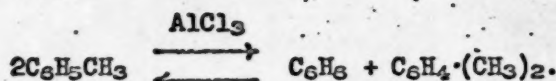
EXPERIMENTAL

Reactions of Methylcyclohexane in the Liquid Phase in Presence of Aluminum Chloride

Pure synthetic methylcyclohexane, b.p. 99.8° at 736 mm, n_D^{20} 1.4225 and d_4^{20} 0.7692, was taken for the experiments. The reaction was carried out in a three-necked flask provided with a mechanical stirrer and a long reflux condenser with a calcium chloride tube. The temperature of the reaction mixture was maintained at 80° by means of an oil-bath.

The time of the treatment of methylcyclohexane in contact with aluminum chloride varied from 4 to 24 hr. In different experiments the amount of aluminum chloride was varied over the range 4 to 20% on the weight of methylcyclohexane taken. Two series of experiments were carried out. The conditions employed in the first series are shown in Table 1. In no case was the evolution of gaseous products observed; the hydrocarbon and the aluminum chloride did not change appreciably in color.

TABLE 1

Conditions employed in the first series of experiments with methylcyclohexane

No. of expt.	Amt. of methylcyclo-hexane taken (g)	Amt. of aluminum chloride taken (%)	Duration of experiment (hr)	Amount of catalyzate obtained	
				(g)	(%)
1	490	4	4	472.5	96.4
2	100	4	8	94.0	94.0
3	220	4	20	206.6	93.9
4	70	8	4	66.0	94.3

At the end of the reaction the hydrocarbon layer was poured off from the aluminum chloride and washed in a separating funnel, first with a 10% solution

of caustic soda and then with water; it was dried over calcium chloride. The refractive indices of the catalyzates obtained varied inappreciably (1.4230- 1.4238) and differed little from the refractive index of the original methyl- cyclohexane. All the catalyzates were fractionally distilled using a column with a metal filling and with an efficiency of 28 theoretical plates. Independently of the conditions under which the experiments were carried out, they all yielded fractions boiling in the range 88-100° at 752 mm. The corresponding fractions (88-95°, 95-98°, 98-99° and 99-100°) of the catalyzates from all the four experiments were united and again fractionally distilled in the same column.

The results obtained are given in Table 2.

TABLE 2

Results of the Second Fractionation at 750 mm of the Fractions Obtained from the Catalyzates of the First Series of Experiments[1]

Fraction No.	Boiling point (°C)	Amount (g)	n_D^{20}	d_4^{20}	Yield of fraction (% of united catalyzates)
1	80.5-90	4.6	1.4125	0.7538	0.56
2	90-91	12.5	1.4100	0.7507	1.54
3	91-95	8.6	1.4145	0.7565	1.00
4	95-98	18.8	1.4220	0.7602	2.30
5	98-99	28.5	1.4228	0.7680	3.50
6	99-100.2	713.8	1.4235	0.7691	87.90
	Residue	25.5			3.10

[1] For the second fractionation, in all 837.0 g of the separate fractions of the catalyzates was taken.

The residue (25.5 g) obtained in the second distillation of the catalyzate fractions, on subsequently distilling over sodium (745 mm), came over within the range 99.5-100°. The new small residue (about 2 g) was a dark-brown resinous mass.

As will be seen from Table 2, the first 3 fractions do not differ essential- ly in their properties from the original methylcyclohexane. Judging from its initial boiling point, fraction 1 may contain a certain amount of cyclohexane to- gether with possible dimethylcyclopentanes.

Fraction 2 (90-91°) is very close in its properties to 1,3- and 1,2-dimethyl- cyclopentanes. Thus Zelinsky [6] gives the following constants for 1,3-dimethyl- cyclopentane: b.p. 90.6-90.8°; n_D^{20} 1.4096; d_4^{20} 0.7543; 1,2-dimethylcyclopentane, according to Chavanne [7], has: b.p. 90.95° at 741 mm, n_D^{20} 1.4093 and d_4^{20} 0.75137.

Fraction 3, evidently, is an intermediate one; it was not investigated furth- er.

In order to elucidate the chemical nature of the hydrocarbons entering into the composition of these fractions, they were subjected to Zelinsky's catalytic dehydrogenation treatment. Platinized silica gel was used as catalyst (10% Pt). Each fraction was passed 2 to 3 times over the catalyst at 300-305° until the re- fractive index did not change further. After the aromatic hydrocarbons in the catalyzates formed had been estimated, they were removed by means of sulfonation. Fractions 1 and 2 were then again isomerized in presence of aluminum chloride. The isomerates obtained, after suitable treatment, were dehydrogenated over the same catalyst. The results of the investigation of the first four fractions separated from the united isomerizate are given in Table 3.

TABLE 3

Investigation of the Products of the Reaction of Methylcyclohexane in Contact with
Aluminum Chloride
(First Series of Experiments)

Frac- tion No.	Properties of the original fraction			Properties of fraction after dehydro- genation		
	Boiling range, °C	n_D^{20}	d_4^{20}	n_D^{20}	d_4^{20}	Content of aro- matic hydro- carbons (%)
1	80.5-90	1.4125	0.7538	1.4160	–	3.3
2	90-91	1.4100	0.7507	1.4105	0.7498	Traces
3	91-95	1.4145	0.7565	(a)1.4235 (b)1.4335 (c)1.4345	– – –	28.3
4	95-98	1.4220	0.7602	(a)1.4495 (b)1.4650 (c)1.4770 (d)1.4935	– – – –	94.0

As will be seen from this table, on passing the 80.5-90° fraction over
Pt-silica-gel, its refractive index changes to an insignificant extent. There
was 3.3% of aromatic hydrocarbons, evidently benzene, in the catalyzate. The
benzene would be formed from cyclohexane, which could arise from methyl-group
transfer among methylcyclohexane molecules. Owing to the insignificant a-
mount of this fraction, we did not succeed in separating and identifying ben-
zene.

It will be seen also from Table 3 that the refractive index of the 90-91°
fraction remained practically unchanged after dehydrogenation. In the cata-
lyzate obtained, no aromatic hydrocarbons could be detected. In order to con-
firm the natural supposition that this fraction contains mainly cyclopentane
derivatives, the catalyzate obtained was isomerized in presence of AlCl₃ at
80° and then catalytically dehydrogenated at 300°. The results of the esti-
mation of aromatic hydrocarbons in the condensate obtained confirmed our sup-
position.

After repeating the catalytic dehydrogenation of fraction 3 (91-95°)
three times, a condensate containing 28.3% of toluene was obtained, which
points to the presence in the fraction of about 30% of unchanged methylcyclo-
hexane. After the dehydrogenation of fraction 4 (95-98°), 94% of aromatic
hydrocarbons was found in the catalyzate. It therefore follows that this
fraction is almost unchanged methylcyclohexane.

Reactions of Methylcyclohexane in Presence of an Increased Amount (to 20%) of Aluminium Chloride

The second group of experiments with methylcyclohexane was carried out in
the same apparatus under conditions analogous to those used in the first series
of experiments, apart from the amount of AlCl₃ taken, which was 20% of the weight

TABLE 3 (Continued)

Investigation of the Products of the Reaction of Methylcyclohexane in Contact with
Aluminum Chloride
(First Series of Experiments)

Properties of the catalyzate after removal of aromatics		Properties of the catalyzate freed from aromatics and then isomerized over AlCl₃		Properties of the isomerizate after dehydrogenation		Properties of the aromatic-free residue	
n_D^{20}	d_4^{20}	n_D^{20}	d_4^{20}	n_D^{20}	Content of aromatics, %	n_D^{20}	d_4^{20}
1.4117	0.7531	1.4140	0.7568	1.4170	15.0	1.4080	0.7460
1.4095	0.7496	1.4210	0.7660	(a)1.4680			
				(b)1.4870	87.0	1.4090	0.7492
1.4115	0.7492	1.4190	–				
1.4175	–	–					

TABLE 4

Results of the Second Fractionation (at 755 mm) of the United Fractions of the
Catalyzates of the Second Group of Experiments

Fraction No.	Boiling range (°C)	Amount (g)	n_D^{20}	d_4^{20}	Yield of fraction	
					On original methylcyclohexane	On the total products of the second distillation
1	82-87	4.4	1.4050	0.7515	0.6	0.7
2	87-89	26.2	1.4113	0.7499	3.3	3.9
3	89-91	10.5	1.4105	0.7504	1.3	1.6
4	91-98	20.0	1.4210	0.7660	2.5	3.0
5	98-99	35.0	1.4229	0.7683	4.4	5.2
6	99-100.2	568.0	1.4230	0.7692	72.0	85.2
7	124-131	2.4	1.4230	0.7606	0.30	0.4

of hydrocarbon taken, and the duration of the reaction, which was increased to
24 hr. Two experiments were carried out in which methylcyclohexane was treated
with AlCl₃ under completely identical conditions. In the first of these (No.5),
400 g of methylcyclohexane was taken, in the second, 390 g. The two isomerizates obtained were first distilled separately through the same column of 28
theoretical plates. Fractions boiling within the range 82-100° at 755 mm were
separated.

Fractions boiling in identical ranges (82-87; 87-89; 89-91; 91-98; 98-99°) were then united and again fractionated through the same column. The results obtained in the second distillation are given in Table 4.

Fractions 1, 2, and 7 were catalytically dehydrogenated at 300° (see Table 5). The contents of aromatic hydrocarbons in the catalyzates obtained were determined by the sulfuric acid method. In the catalyzate of fraction 1 (82-87°), 19% of aromatic hydrocarbons was found. According to its constants, the residue of this fraction after freeing from aromatics was 1,3-dimethylcyclopentane.

After fraction 2 (87-89°) had been passed over platinized silica gel, its refractive index suffered an inappreciable change, which gives us reason to consider that it consists mainly of dimethylcyclopentanes; its physicochemical properties are in accord with this view.

In order to elucidate the nature of fraction 7 (124-131°), having n_D^{20} 1.4230 and d_4^{20} 0.7606, it was subjected to catalytic dehydrogenation. After two passages over Pt — silica-gel, a catalyzate having n_D^{20} 1.4933 and d_4^{20} 0.8623 was obtained. Fractional distillation of this catalyzate at 740 mm yields the fractions:

Fr. 1, b.p. 111-116° – 0.21 g;
Fr. 2, b.p. 117-135° – 0.24 g.

Both fractions were oxidized by Ullmann's method [8].

TABLE 5

Investigation of the Products of the Reaction of Methylcyclohexane in Presence of 20% AlCl₃

Fraction No.	Boiling range (°C)	n_D^{20}	d_4^{20}	After dehydrogenation			Properties of the catalyzate after removal of aromatics	
				n_D^{20}	d_4^{20}	Content of aromatics (%)	n_D^{20}	d_4^{20}
1	82-87	1.4050	0.7515	1.4145	–	19.0	1.4035	0.7452
2	87-89	1.4113	0.7499	1.4118	–	2.0	1.4087	0.7482
7	124-131	1.4230	0.7606	(a)1.4898	–			
				(b)1.4933	0.8623			

The separation of the acids obtained was carried out by the method described by Moldavsky, Kamusher, and Kobylskaya [9]. As a result of the oxidation of the 111-116° fraction, benzoic acid, m.p. 121°, was obtained. From the products of the oxidation of the 117-135° fraction, after separation of benzoic acid, the methyl ester of isophthalic acid [9], m.p. 62-64°, was obtained. The presence of isophthalic acid in the oxidation products of this fraction indicates the presence of m-xylene in the catalyzate. The m-xylene is evidently formed as a result of the methyl-redistribution reaction of methylcyclohexane in presence of aluminium chloride.

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Reactions of Toluene in the Liquid Phase in Presence of Aluminum Chloride

In the experiments with toluene, the question of the possibility of the formation of benzene and xylene in presence of aluminum chloride under our conditions was of fundamental interest. The toluene taken for the experiments was first distilled through a column (see above); it had the following properties: b.p. 109.5-110° at 750 mm; n_D^{20} 1.4965; d_4^{20} 0.8666.

The reaction was carried out under the conditions used for methylcyclohexane, the time in contact with aluminum chloride being 8 hr. In different experiments the amount of aluminum chloride was varied from 4 to 10% on the weight of toluene taken.

As it was found that the catalyzates obtained by the use of various amounts of $AlCl_3$ did not differ essentially from one another, they were all united for further investigation. In no experiment was the evolution of gaseous products observed. The color of the hydrocarbon did not change appreciably, but a small amount of a dark-colored resin-like layer was formed on the bottom of the flask. 1426 g of toluene was treated in three batches with aluminum chloride. 1123 g of a hydrocarbon layer and 338 g of a toluene – aluminum chloride complex were isolated. The hydrocarbon layer, after being washed and dried with calcium chloride, was fractionated over sodium through the column at 752 mm. Three fractions were separated; their properties are given in Table 6.

TABLE 6
Results of the Action of $AlCl_3$ on Toluene

No.of fraction	Boiling range (°C)	n_D^{20}	d_4^{20}	Weight (g)	Yield of fraction (%)	
					On original toluene	On isomerizate obtained
1	80-108	1.4980	0.8724	18.8	1.3	1.7
2	108-110	1.4965	0.8666	948.0	66.5	84.4
3	110-141	1.4975	0.8683	56.0	4.0	5.0

Fraction 1 (80-108°) was again fractionated under the same conditions; 12.5 g of benzene, b.p. 79.5-80° at 753 mm; n_D^{20} 1.4995; d_4^{20} 0.8755, was isolated from this fraction.

The properties of Fraction 2 indicate it to be almost unchanged toluene (108-111°). Fraction 3 (110-141°) was separated by fractionation through the column into five fractions, the properties of which are given in Table 7.

The data in Table 7 show that, as a result of further fractionation of the 110-141° distillate, xylene fractions boiling over the range 136-141° have been separated; the total quantity of these (without the residue) was 29.3 g, or about 2%, calculated on the original toluene. In order to determine the structures of the xylenes, the fractions obtained (136-139°, 139-141°, and also the part boiling at 141°) were oxidized by Ullmann's method [8]. The relative amounts of isomers in each fraction was established by separation of the acids obtained by oxidizing that particular fraction. The separation of the acids was carried out by the method described by Moldavsky and coworkers [9]. The results of the analysis of the oxidation products are presented in Table 8.

It follows from the results given in Table 8 that the 136-139° fraction consists essentially of m-xylene, the 139-141° fraction contains a considerable

TABLE 7

Results of the Refractionation of the 110-141° Fraction

No.of fraction	Boiling range (°C at 756 mm)	Amount (g)	n_D^{20}	d_4^{20}
1	107.5-109.5	20.4	1.4955	0.8655
2	126-136	1.3	1.4960	0.8650
3	136-139	16.9	1.4965	0.8656
4	139-141	3.9	1.5000	0.8704
5	141	8.5	1.5010	0.8855
	Residue	3.0		

TABLE 8

Results of the Analysis of the Oxidation Products of the Xylene Fractions

Boiling range of fraction	Amounts of the acids obtained (% of total quantity of oxidation products)			
	Benzoic	Phthalic	Isophthalic	Terephthalic
136-139	0.5	3.4	82.5	13.6
139-141	0.4	29.8	63.2	6.6
141	–	75.7	19.0	5.3

amount of m-xylene (63.2%) together with appreciable amounts of o- and p-xylenes, and the part of the catalyzate boiling at 141° consists mainly of o-xylene, though even here there is appreciable admixture with m-xylene.

SUMMARY

1. A study has been made of the reactions of methylcyclohexane in the liquid phase in presence of anhydrous aluminum chloride at 80° under normal pressure.

2. It has been established that when methylcyclohexane reacts with aluminum chloride under these conditions it not only isomerizes with shrinkage of the ring into dimethylcyclopentane, but also undergoes the process of methyl-group redistribution to a small extent and, as a result, dimethylcyclohexane and cyclohexane are formed.

3. It has been shown that in the reaction of aluminum chloride with toluene under analogous conditions there is a redistribution of methyl groups resulting in the formation of benzene and a mixture of isomeric xylenes.

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THE CATALYTIC HYDROCONDENSATION OF CARBON MONOXIDE WITH OLEFINS

COMMUNICATION 7. EFFECT OF THE CARBON MONOXIDE CONCENTRATION ON THE HYDROCONDENSATION REACTIONS OF CARBON MONOXIDE WITH PROPENE AND WITH n-BUTENE

Ya. T. Eydus, N. D. Zelinsky, K. V. Puzitsky, and N. I. Ershov

We have previously shown that equimolecular mixtures of n-butene and hydrogen [1], propene and hydrogen [2], and ethylene and hydrogen [3], containing 4-7% of carbon monoxide, undergo catalytic hydrocondensation with formation of a liquid product that consists of saturated aliphatic hydrocarbons and olefins. For an ethylene-hydrogen mixture it was shown that this reaction does not occur in the complete absence of carbon monoxide in the original gas mixture, the ethylene being then hydrogenated to ethane. An ethylene-hydrogen mixture containing 15% of carbon monoxide, e.g. $1CO:2H_2:3C_2H_4$, undergoes also the hydrocondensation reaction [4]. About 80% of the original ethylene participates in the formation of the condensate, and 20% is hydrogenated to ethane. The liquid condensate, which is essentially a mixture of aliphatic hydrocarbons, contains a small admixture of organic compounds containing oxygen [5].

EXPERIMENTAL

The present work has as its object the investigation of the effect of the carbon monoxide concentration on the hydrocondensation reactions of carbon monoxide with propene and with n-butene. The apparatus, procedure, and experimental conditions, and also the preparation, purification, and analysis of the gases, were the same as in the previous work [1,2]. For the preparation of the initial gas mixtures, 95% propene, prepared by the dehydration over aluminum oxide of isopropyl alcohol, b.p. 81-81.5°; d_4^{20} 0.7898; n_D^{20} 13779; Found MR_D 17.53; calculated MR_D 17.58, was used. After condensation, this propylene was redistilled through a Davis column over the range -46.5 to -45°. The butene used in the experiments was prepared from n-butyl alcohol as in the previous work [1].

The Experimental Results and their Discussion

1. Experiments with propene. Experiments, analogous to those carried out with ethylene [3], were directed to the study of the dependence of the degree of polymerizability of the propene-hydrogen mixture on the carbon monoxide concentration, which varied over the range 0-22% of the initial gas mixture. The results are given in Tables 1, 2 and 3.

The experiments were carried out over freshly reduced catalysts 21, 22, 23, 24, 25, 26, 27 and 28 with a space velocity of 80-100 liter/liter hr.

Experiment 148 (Table 1) was carried out with a gas mixture prepared from propene that had been twice condensed at -70° with removal of the gaseous residue by pumping, then passed in the gaseous condition, after the usual purification, through three columns containing ammoniacal cuprous chloride, the gas being

forced through the Schott filters in the bases of the columns. This was done with the aim of freeing the gas completely from carbon monoxide, which may be formed as a by-product during the dehydration of the alcohol, owing to decomposition of the aldehyde. Actually, the amount of carbon monoxide in the initial gas of Experiment

TABLE 1

Cat-al-yst	Expt. No.	Dura-tion of expt., hours	CO in init-ial mix-ture, %	Volume ratio $C_3H_8:H_2$ in initial mixture	Con-tract-ion, %	Yield (ml/m³)			Volume ratio H/L	Yield of oil (H + L) ml/liter per hour
						of heavy oil (H)	of light oil (L)	of oil (H + L)		
22	148	12.0	0.0	1.0	51.2	0.0	27.0	27.0	0.0	1.8
22	149	12.0	0.2	1.0	44.2	0.0	20.5	20.5	0.0	1.4
22	150	6.0	1.3	1.0	51.0	12.0	84.0	96.0	0.14	6.5
23	152	5.0	1.8	1.1	47.0	32.1	128.4	160.5	0.25	12.5
24	153	6.0	2.0	0.9	50.5	23.9	161.7	185.6	0.15	12.3
22	151	6.0	2.8	1.0	44.0	40.0	131.6	171.6	0.30	11.9
26	155	6.0	3.7	1.4	52.4	43.6	217.8	261.4	0.20	26.6
25	154	6.0	3.7	1.1	47.4	97.7	293.1	390.8	0.33	29.4
21	147	12.0	5.7	1.1	66.4	239.8	337.7	577.5	0.71	35.5
21	144	11.2	6.2	0.9	69.5	277.4	275.1	552.5	1.01	36.1
27	156	6.0	11.6	1.6	52.2	216.5	97.0	313.5	2.23	30.6
28	161	5.0	13.6	1.5	44.8	125.4	66.0	191.4	1.90	19.7
27	157	6.0	14.2	1.2	39.0	102.3	40.1	142.4	2.55	13.0
27	158	6.0	15.4	1.4	32.9	85.8	18.5	104.3	4.63	10.6
28	160	6.0	18.4	1.8	40.2	98.2	30.5	128.7	3.22	11.7
28	159	6.0	22.0	1.9	38.5	82.5	29.7	112.2	2.78	10.6

TABLE 2

Expt. No.	Composition of initial gas (vol.%)[1]				Composition of effluent gas (vol.%)[2]				
	C_3H_8	H_2	CO	N_2	C_3H_8	H_2	CO	C_3H_8	N_2
155	53.2	36.0	3.7	7.0	45.8	8.8	0.0	32.3	13.0
147	47.3	43.2	5.7	2.8	17.8	7.1	1.3	57.1	15.2
144	42.2	46.6	6.2	4.6	0.5	1.4	0.5	72.6	23.9
156	49.6	30.9	11.6	6.0	62.4	7.6	1.8	16.5	7.3
161	49.4	30.2	13.6	3.5	66.4	9.0	7.2	9.9	6.5
157	43.0	36.6	14.2	4.8	58.4	15.6	8.4	7.8	8.2
158	46.2	32.3	15.4	5.0	58.8	17.0	11.6	4.6	6.4
160	48.0	26.5	18.4	5.5	66.4	6.6	13.0	5.7	6.1
159	48.0	25.0	22.0	3.9	65.2	4.4	15.4	5.7	5.5

[1] The defect from 100% must be regarded as oxygen.

[2] The defect from 100% must be regarded as oxygen and carbon dioxide, the combined content of which attained 2-3% in some of the gases.

148 was nil with a possible error of 0.05%, the method of estimation being more accurate than the usual gas-analysis method. In this experiment, as also in Experiment 149, in which a gas mixture containing 0.2% of carbon monoxide was used, the yield of heavy oil was nil and that of light oil extremely small (20-27 ml/m³, or 1.4-1.8

TABLE 3

No. of experiment	CO in initial gas (%)	Amount that reacts (%)			Ratio of the reacting volumes of	
		C_3H_6	H_2	CO	H_2 and CO (H_2/CO)	C_3H_6 and CO (C_3H_6/CO)
155	3.7	60.3	88.7	100.0	7.7	8.7
147	5.7	87.5	90.3	92.6	7.4	7.9
144	6.2	99.7	99.1	97.0	9.7	9.1
156	11.6	39.3	88.3	91.1	2.5	1.8
161	13.6	26.0	84.6	70.9	2.7	1.3
157	14.2	17.0	74.0	63.9	2.9	0.8
158	15.4	14.5	64.7	49.2	2.7	0.8
160	18.4	17.3	85.4	58.0	2.1	0.7
159	22.0	16.2	89.0	57.0	1.8	0.6

ml/liter hour, to 577.5 ml/m³, . or 36.1 ml/liter hour, also the volume ratio of heavy to light oil increases from 0.0 to 1.0, which also indicates an increased degree of condensability with increase in carbon monoxide concentration. An analogous relation is observed also for the % of propene that has reacted; this rises from 60.3 to 99.7 when the carbon monoxide concentration rises from 3.7 to 6.2% (Table 3).

With further increase in the carbon monoxide concentration, the yield of liquid condensate and the % of propene that has reacted begin to fall sharply, and at 14% CO and higher they remain constant at a fairly low level: 10.6-13 ml/liter hour for the yield of oil and 14.5-17.3% for the amount of propene that has reacted. Thus, in contrast to ethylene [4,5], propene does not undergo the hydrocondensation reaction with carbon monoxide when the content of the latter is equal to or in excess of 14-15%. In Figure 1 these relationships are shown graphically (Curves a and b).

It will be seen from Table 3 and Figure 1 (Curve c) that the ratios of the reacting volumes of the components, C_3H_6/CO and H_2/CO, are quite different in the regions of high and of low carbon monoxide concentration. In the low-concentration region (up to 6%), these quantities have the values 7.9-9.1 and 7.4-9.7 respectively, i.e., on the average 8-9. At carbon monoxide concentrations of 14% and greater, the values fall sharply to 0.6-1.8 and 1.8-2.9 respectively. It will be seen from Table 1 that a certain degree of variability in the initial volume ratio C_3H_6/H_2 has no appreciable effect on the way in which the process is found to depend on the carbon monoxide concentration.
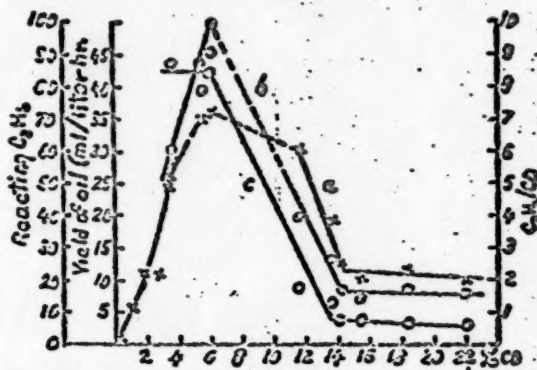
Fig. 1

The fraction of reacting hydrogen remains almost independent of the carbon monoxide concentration and has the value of 85-99%. Only for a carbon monoxide concentration of 14-15% does the fraction of reacting hydrogen fall somewhat (to

65-74%). As regards the amount of reacting carbon monoxide, this falls continuously as the CO concentration increases, but in absolute amount, carbon monoxide reacts to an extent that is 1.5-2 times greater in regions of high concentration than in regions of low concentration. This is deduced from a comparison in various experiments of the product obtained by multiplying the fraction of carbon monoxide in the initial gas mixture by the fraction of reacting carbon monoxide in the same experiment.

It is evident from the results obtained that completely different processes occur in the regions of low and of high carbon monoxide concentration. In the first case, propene undergoes the processes of hydrocondensation with carbon monoxide and of hydropolymerization, and these become more intense as the carbon monoxide content of the mixture increases. Here there is a manifest resemblance between propene and ethylene. In the second case this process is suppressed; less than 15% of the original propene takes part in it. The main reaction is between carbon monoxide and hydrogen, evidenced by the yield of oil, 110-140 ml/m^3 or 10-13 ml/liter hour, and, particularly, by the ratio of the reacting volumes of hydrogen and carbon monoxide (H_2/CO = about 2). Here we already find a difference between the behavior of propene on the one hand and of ethylene on the other, for the latter very readily undergoes hydrocondensation with carbon monoxide when the content of the latter in the initial mixture is high [4,5]. This difference is evidently determined by the existence of adsorption and steric difficulties in the case of propene.

2. Experiments with n-Butene. In Table 4 the results are given of experiments on the hydrocondensation of an equimolecular mixture of n-butene and hydrogen in absence of carbon monoxide at 190° under atmospheric pressure.

TABLE 4

Catalyst	Experiment No.	Duration of experiment, hours	Space velocity, liter/liter hour	CO in original gas (%)	Contraction (%)	Yield (ml/m³)				Yield of oil (H + L, in ml/liter hr)
						Heavy oil (H)	Light oil (L)	H + L	Water	
Glass beads	173	4.0	94	0.0	0.0	0.0	0.0	0.0	0.0	0.0
34	171	5.5	90	0.00	57.1	0.0	23.5	23.5	0.0	2.0
34	172	6.0	100	0.00	56.2	0.0	25.9	25.9	0.0	2.3
35	174	24	60	0.0	47	6.0	51.5	57.5	4.5	3.1
35	175	12	68	0.0	55	8.7	38.5	47.2	5.3	2.7
35	176	10.7	75	2.5	53	112.7	85.5	198.2	15.0	13.5

Experiment 173 was carried out over glass beads and was for control purposes. The remaining experiments were carried out over freshly reduced catalysts 34 and 35.

It will be seen from Table 4 that in absence of carbon monoxide the hydrocondensation of n-butene does not occur to an appreciable extent. Experiments 171 and 172 were carried out with mixtures containing butene that had been carefully purified from carbon monoxide by liquefying it several times and pumping off the unliquefied gaseous residue on each occasion. In these experiments the yield of oil was 24-26 ml/m^3, and no heavy oil was obtained. In Experiments 173 and 174 the original butene was not specially purified from carbon monoxide, and

TABLE 5.

Cat-alyst	Ex-peri-ment No.	Dur-ation of exp. (hr)	Space vel-ocity (liter/liter hour)	CO in orig-inal gas (%)	Vol. ratio C₄H₈/H₂ in initial gas	Con-trac-tion (%)	Yield (ml/m³) Heavy oil (H)	Light oil (L)	H + L	Water	Yield of oil (H + L, in ml/liter hour)	Vol. ratio H/L
36	177	6	86	5.8	0.85	61.1	106.1	283.2	389.3	28.3	30.5	0.37
36	178	5	97	5.5	0.98	67.1	158.6	377.6	536.2	37.7	48.0	0.42
36	179	5	98	4.6	1.16	63.0	149.2	373.1	522.3	44.6	46.6	0.39
36	180	6	93	13.6	1.27	57.7	144.1	32.7	176.8	78.5	15.0	4.40
36	181	5	92	14.0	1.38	54.5	160.0	39.7	199.7	103.1	16.6	4.03
36	182	5	107	15.2	1.72	53.0	116.6	68.5	185.1	68.5	18.0	1.70
36	183	5	86	5.8	0.87	64.7	84.9	235.0	319.9	42.5	26.6	0.36
36	184	6	89	4.0	1.19	60.0	41.2	310.3	351.5	20.6	28.3	0.13
36	185	6	81	6.0	1.13	63.7	52.5	375.6	428.1	22.4	31.6	0.14
36	186	6	88	5.6	1.00	61.0	34.8	382.6	417.4	41.7	33.3	0.09
36	187	5	99	12.2	1.00	57.4	89.1	222.7	311.8	59.4	28.0	0.40
36	188	6	88	14.8	1.38	50.7	76.3	97.2	173.5	104.3	13.9	0.78
36	189	5	101	15.8	1.47	53.1	72.5	145.0	217.5	79.6	20.0	0.50
36	190	6	99	5.6	1.23	58.4	80.1	277.1	357.2	43.1	32.2	0.28

in these experiments the yield of oil rose to 47-58 ml/m³. Thus n-butene, like ethylene and propene, does not undergo the hydrocondensation reaction in absence of carbon monoxide. It will be seen from the results of Experiment 176 (Table 4) that already in presence of 2.5% of carbon monoxide in the butene-hydrogen mixture this reaction is promoted: the yield of oil attains 198.2 ml/m³. the ratio of heavy to light oil being 1.32.

In Tables 5, 6, and 7 results are given of experiments on the hydrocondensation of n-butene over one given catalyst, 36, in presence of alternately low (4-6%) and high (14-15%) concentrations of carbon monoxide. As will be seen from Table 5, the yield of oil, on going from low to high concentrations, falls sharply, while the ratio of heavy to light oil increases greatly. Thus the yield of oil is 46.6 and 15 ml/liter hour in Experiments 179 and 180 respectively, 26.6 and 18.0 in Experiments 183 and 182, and 32.2 and 20.0 in Experiments 190 and 189. In the same experiments the volume ratios of heavy and light oils are 0.39 and 4.40; 0.36 and 1.70; 0.28 and 0:50. From Table 5 it will be seen that the act-ivity and condensing propensity of the catalyst fall as its participation in the process increases. This follows also from the results in Table 7 when the part taken by butene in the reaction is compared for a given range of carbon monoxide concentrations. Thus in Experiments 177-178 the fraction of butene reacting is 90-94%, in Experiments 183-186 it is 76-80%, and in Experiment 90 it is 64%. However, on going from low carbon monoxide concentrations to high this fraction is considerably less: in Experiments 180-182 it is 42-54%, and in Experiments 188-189 it is 35.5-42.4%. An intermediate position is occupied by Experiment 187, in which the initial gas mixture contained 12.2% of carbon monoxide, i.e. was characterized by an intermediate carbon monoxide concentration. In this experiment the yield of oil was 28.0 ml/liter hour and the fraction of butene reacting was 55%. Regions of differing carbon monoxide concentrations differ in the ratios of reacting components H₂/CO and C₄H₈/CO. In the low-concentration range these ratios have values from 6 to 9, and in the high-concentration range their values vary around 2.

TABLE 6

Expt. No.	Composition of original gas (vol.%)[1]			Composition of effluent gas (vol.%)[2]		
	C_4H_8	H_2	CO	C_4H_8	H_2	CO
177	38.4	44.7	5.8	5.8	18.9	0.0
178	41.3	42.2	5.5	12.4	7.2	0.0
180	45.8	36.2	13.6	49.2	9.2	2.4
181	44.5	32.1	14.0	54.0	16.4	5.6
182	48.2	28.3	15.2	59.2	8.8	7.2
183	40.0	46.0	5.8	22.8	5.6	1.6
184	48.0	40.3	4.0	26.5	6.9	0.0
185	46.0	40.6	6.0	28.4	6.4	0.0
186	44.0	43.8	5.6	26.4	10.0	0.0
187	40.6	40.0	12.2	43.2	15.0	0.0
188	45.4	33.0	14.8	59.2	12.0	6.4
189	46.4	31.7	15.8	58.0	12.2	9.2
190	48.6	39.4	5.6	41.6	8.0	0.4

[1] As a rule, there was about 1 liter of N_2 in the original and effluent gases.
[2] The effluent gas contained 1-2% CO_2

TABLE 7

Expt. No.	CO in initial mixture (%)	Amount that reacted (%)			Amount formed (%)		Ratio of reacting volumes of:	
		C_4H_8	H_2	CO	C_4H_{10} from the reacting hydrogen	C_4H_{10} from the reacting C_4H_8	H_2 and CO (H_2/CO)	C_4H_8 and CO (C_4H_8/CO)
177	5.8	94.1	83.7	100	38.8	40.2	6.82	6.59
178	5.5	90.2	94.4	100	46.2	49.4	7.27	6.80
180	13.6	54.7	89.3	92.5	23.9	30.8	2.57	2.00
181	14.0	44.6	76.8	81.9	18.5	23.0	2.15	1.73
182	15.2	42.1	85.7	77.8	12.4	14.7	2.04	1.73
183	5.8	79.8	95.8	88.1	32.1	44.3	8.43	6.10
184	4.0	78.2	93.2	100	45.3	45.5	9.40	9.39
185	6.0	77.5	93.3	100	39.9	42.8	6.35	5.92
186	5.6	76.4	91.0	100	33.5	39.7	7.16	6.04
187	12.2	54.9	84.1	100	22.7	34.2	2.76	1.83
188	14.8	35.5	82.1	78.7	12.9	21.5	2.32	1.38
189	15.8	42.4	75.5	73.3	10.6	13.0	2.07	1.69
190	5.6	64.1	72.6	96.8	28.8	33.3	6.65	5.75

Thus, the behavior found in propene is observed also for the case of n-butene. The concentration of carbon monoxide has a powerful influence on the hydrocondensation reaction of the olefin, and at a carbon monoxide concentration of 15% this process is suppressed to a considerable extent. The causes for this behavior probably lie, as in the case of propene, in difficulties of an adsorption and steric nature. This question is of great interest and requires further investigation.

SUMMARY

1. An investigation has been made into the effect of the concentration of carbon monoxide on its hydrocondensation with propene and with n-butene.

2. It has been established that, in absence of carbon monoxide, hydrocondensation does not occur in propene – hydrogen and butene – hydrogen mixtures.

3. The highest rate for the reaction of the hydrocondensation of propene or butene with carbon monoxide occurs when 6-8% of the latter is present in the original gas mixture.

4. When the carbon monoxide concentration in the original mixture is 15-20%, the process of hydrocondensation with propene or butene is greatly retarded; this stands in contrast to the course of the process of hydrocondensation with ethylene.

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THE SPLITTING-OFF OF THE ELEMENTS OF HYDROGEN HALIDE

FROM MONOHALO DERIVATIVES OF HYDROCARBONS OF THE SERIES C_nH_{2n+2}

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Markovnikov's rule [1] for the order of the addition of the elements of hydrogen halide to hydrocarbons of the series C_nH_{2n}, according to which "the halogen adds to the most hydrogenated carbon, i.e. to that which is the most subject to the influence of other carbon atoms", is confirmed by numerous facts and is generally accepted. Indications in the literature [2] of a partial change in the order of addition of HBr to isobutylene, trimethylethylene, and isopropylethylene, contrary to Markovnikov's rule, is to be explained by the presence of traces of peroxides, which cause this sort of anomaly. According to Delacr's results [3], 3,3-dimethyl-1-butene, on adding HBr, gives the primary instead of the expected secondary bromide, and this also was explained by the action of traces of peroxides. Whitmore and Homeyer [4] showed that HBr adds on to 4,4-dimethyl-1-pentene in a manner contrary to Markovnikov's rule – if we assume that in this case peroxides are absent.

Markovnikov [8] established that when hydrogen halide splits off from an alkyl monohalide the hydrogen that splits off comes not from the carbon atom to which the halogen is attached, but from the adjacent one. This rule also is confirmed by numerous facts, not only in the case of monohalides, but also, as Eltekov [5] has shown, in the case of polyhalo compounds.

Markovnikov's conclusion, that "when the elements of hydrogen halide separate from the halo compound, they always come from adjacent carbons, and the least hydrogenated carbon, even if this is connected further to highly hydrogenated carbons, has the last tendency to lose hydrogen", has been found to be erroneous in the last part of the statement. The reason for this was the inadequacy of the experimental data obtained by Markovnikov in his study of the splitting of HI from 2-iodo-3-methylbutane by the action of alcoholic caustic potash. As is well known, Zaytsev [6], on the basis of numerous facts, came to the opposite conclusion – "when a carbon that is linked to iodine is linked also to carbons having different degrees of hydrogenation, the least hydrogenated carbon has the greatest tendency to lose its hydrogen." Vagner [7], who examined the splitting of HI from 2-iodobutane, 2-iodo-2-methylbutane, and secondary hexyl iodide under the action of alcoholic potash, showed that Zaytsev's rule expresses only the predominating direction of the reaction. In those cases where Vagner showed that HI is split off in two ways, the carbon atom linked with iodine is adjacent to methyl and methylene. But if the iodine is attached to a carbon that is linked on the one hand to methyl and on the other to CH, then, according to Favorsky [8], "it is very probable that in the last case the hydrogen of the hydrogen iodide will come exclusively from the CH group." But it should be noted that also these addenda to Zaytsev's rule are based on facts obtained from a study of the halogen derivatives of hydrocarbons that do not contain quaternary carbon atoms.

As is well known, diisobutylene, which was first prepared by Butlerov [9], is a mixture of 80% 2,4,4-trimethyl-4-pentene (α-form) and 20% 2,4,4-trimethyl-3-pentene (β-form):

$$CH_2{=}C{-}CH_2{-}C{-}CH_3 \;+\; CH_3{-}C{=}CH{-}C{-}CH_3$$

CH₃ CH₃ · CH₃ CH₃

80% 20%
(α-form) (β-form)
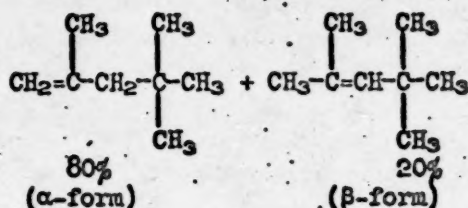
Butlerov [9], by oxidizing diisobutylene with a 5% solution of $KMnO_4$, obtained oxoctenol (epoxyalcohol) (prismatic needles, m.p. 49.5°) and trimethylacetic acid, which are formed only from the β-form of diisobutylene.

On the basis of the amounts of oxoctenol and trimethylacetic acid obtained in the oxidation of diisobutylene by the method of Vagner [7] and Prilezhaev [10], we have derived the quantity of β-form in diisobutylene obtained by different methods. On splitting HCl (I) from 2-Cl(Br,I)-2,4,4-trimethylpentane, then according to Zaytsev we should obtain mainly the β-form of diisobutylene.

By treating 2-Cl(I)-2,4,4-trimethylpentane with alcoholic potash, we obtained as our main product, as the experiments described below will show, the β-form of diisobutylene, i.e. the elements of hydrogen halide are split off from this particular halogen compound in a manner contrary to Zaytsev's rule: the splitting-off of an H atom proceeds mainly at the most hydrogenated carbon atom, i.e. the methyl, and not the methylene. This fact is interesting as an example of a definite change in the order of splitting-off of the elements of hydrogen halide, depending on a change in the chemical structure of the organic halide molecule and therefore on a change in the nature of the mutual effects of the atoms making up the molecule. Is this property of 2-Cl(I)-2,4,4-trimethylpentane — the splitting-off of HCl(I) in a manner contrary to Zaytsev's rule — determined merely by the presence of the quaternary carbon atom, or by the neopentyl group?

According to Markovnikov [1], there is a resemblance between dehydration and the splitting off of hydrogen halide from these compounds. "All that has been said of the splitting off of water is completely applicable also to the splitting off of hydrogen halide." This is indeed confirmed by the facts: as Whitmore [11] has shown, on dehydrating dimethylneopentylcarbinol over an acid catalyst, there is formed a mixture of diisobutylenes containing 80% of the α-form and 20% of the β-form. Comparing these results for the dehydration of dimethylneopentylcarbinol with ours — by the action on 2-Cl(I)-2,4,4-trimethylpentane of alcoholic potash, the β-form of diisobutylene is formed in small quantity — very small in the case of the iodo compound.

According to Whitmore's results, dehydration of 2;2,3-trimethyl-3-pentanol gives 80% of the normal dehydration product, i.e. 2,2,3-trimethyl-3-pentene. According to our results, approximately the same amount of this olefin is obtained by the splitting off of hydrogen halide from the hydriodic ester of this same alcohol, from which it follows that when the halogen is adjacent to a methyl group and to a quaternary carbon atom (tertiary butyl), the elements of hydrogen halide are split off according to the Zaytsev-Vagner rule. However, in 2-Cl(I)-2,4,4-trimethylpentane, the neopentyl group behaves in a special way, causing the hydrogen of the methyl group, and not of the methylene group, to become the more reactive, which is evidenced by the formation of a preponderance of the α-form of diisobutylene on splitting off HCl from the halogen compound indicated.

For investigation we took diisobutylene prepared by the following methods:

1) from isobutyl alcohol by the action of 63% sulfuric acid [12];

2) from tert-butylsulfuric acid (which is prepared by saturating in the cold two volumes of 63% sulfuric acid with one volume of liquid isobutylene) by heating for one hour on the water-bath; yield of diisobutylene, b.p. 100-105°, 62-63%, and of triisobutylene, b.p. 176-179°, 37-38%;

3) by splitting off the elements of hydrogen halide from 2-Cl(I)-2,4,4-trimethylpentane.

The hydrogen halide addition products were obtained by saturating the diisobutylene (cooled in ice) with gaseous HCl(HI). 2-Cl-2,4,4-trimethylpentane had b.p. 144-150°; d_4^{20} 0.8723; n_D^{20} 1.4395; calculated MR_D 44.01; found MR_D 43.70; 2-I-2,4,4-trimethylpentane had b.p. 82°/15 mm; d_4^{20} 1.2866; n_D^{20} 1.4919; calculated MR_D 51.9; found MR_D 52.4.

The properties of the original diisobutylenes are given in Table 1.

TABLE 1

No.	Original diisobutylene	B. p. (°C)	d_4^{20}	n_D^{20}	Found MR_D	Calculated MR_D
1	Diisobutylene prepared from isobutyl alcohol and 63% H_2SO_4	100-104.5	0.7211	1.4069	38.32	38.67
2	Diisobutylene prepared by splitting HCl from 2-Cl-2,4,4-trimethylpentane	100-102.5	0.7193	1.4091	38.57	38.67
3	Diisobutylene prepared by splitting HI from 2-I-2,4,4-trimethylpentane	100-105	0.7306	1.4112	38.13	38.67
4	Butlerov's diisobutylene	100-105	0.7129	1.4095	38.95	38.67

Diisobutylene was oxidized with a 1% solution of $KMnO_4$ according to Vagner [7] and Prilezhaev [10], and the amount of oxoctenol (the epoxyalcohol) and of trimethylacetic acid was determined; these, as pointed out above, are formed only in the oxidation of the β-form of diisobutylene:
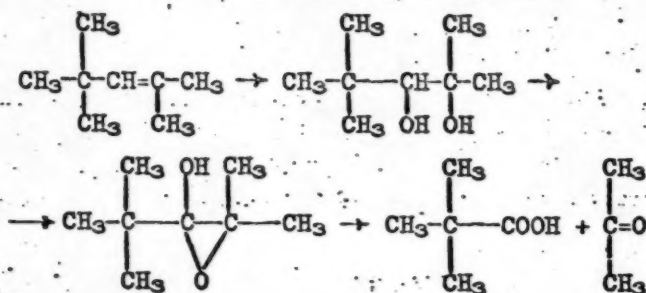
The results of experiments on the oxidation of diisobutylene are given in Table 2, from which it will be seen that diisobutylene obtained from isobutyl alcohol by the action of 63% sulfuric acid contains the least amount of the β-form, since, under the action of sulfuric acid, it isomerizes into 2,3,4- and 2,2,3-trimethylpentene [12].

TABLE 2

No.	Initial product	Weight of diisobutylene taken (g)	Weight of diisobutylene unreacted (g)	Obtained (g)			Oxidized diisobutylene (g)	Yield of oxoctenol on diisobutylene taken (%)	Yield of oxoctenol on diisobutylene oxidized(%)	% β-form in the initial diisobutylene
				Oxoctenol fraction, b.p. 175-179°	Trimethylacetic acid	Glycol				
1	Diisobutylene prepared from isobutyl alcohol and 63% H₂SO₄	21	17.28	0.42	1.00	0.50	3.72	2.30	8.8	6.70
2	Diisobutylene prepared by splitting HCl from 2-Cl-2,4,4-trimethylpentane	21	17.20	1.15	1.00	1.00	3.80	4.25	23.5	10.00
3	Butlerov's diisobutylene .	36.4	10.2	4.7	3.00	3.00	26.2	10.00	14.00	19.00

On splitting off the elements of hydrogen halide from 2-Cl-2,4,4-trimethylpentane, 10% of the β-form of diisobutylene is formed, i.e. half of the amount present in the diisobutylene of Butlerov, and when HI is split off 2-I-2,4,4-trimethylpentane the amount of β-form produced is again small, for only traces of oxoctenol were found in the oxidation products, which confirms that the elements of HCl and HI are split off from these halo compounds in a manner contrary to A.M.Zaytsev's rule.

In all experiments in which diisobutylene was oxidized with 1% KMnO₄, oxoctenol (the apoxyalcohol) was obtained as transparent prismatic needles, m.p. 49-51°.

<div align="center">Analysis of oxoctenol</div>

<div align="center">Found %: C 66.85; 66.63; H 11.29; 11.30.</div>
$C_8H_{16}O_2$. Calculated %: C 66.66;   H 11.11.

Determination of the number of hydroxy groups in oxoctenol according to Chugaev-Tserevitinov:

<div align="center">Found %: OH 10.8</div>
$C_8H_{16}O_2$. Calculated %: OH 11.8.

In the oxidation products, as well as oxoctenol, small quantities were found of trimethylacetic acid and the glycol. B.p. of trimethylacetic acid 162-164°.

Constants of the glycol fraction: b.p. 170-180°; d_4^{20} 0.9033; calculated MR_D 40.68; % hydroxy groups 20; n_D^{20} 1.4249; found MR_D 40.78; calculated % OH - 23.

<div align="center">SUMMARY</div>

1. It is shown that, on splitting off the elements of hydrogen halide by the aid of alcoholic potash from the hydrohalic esters of dimethylreopentylcarbinol [2-Cl(I)-2,4,4-trimethylpentane], the hydrogen that is necessary for the formation

of the hydrogen halide splits off from the most highly hydrogenated carbon atom — from the methyl, and not the methylene group; i.e., contrary to Zaytsev's rule.

2. This departure from Zaytsev's rule concerning the order of the splitting-off of the elements of hydrogen halide from monohalo derivatives of hydrocarbons of the C_nH_{2n+2} series is at present the only exception and is to be explained by the presence of the neopentyl radical; in just the same way the addition of hydrogen bromide to neopentylethylene in a manner contrary to Markovnikov's rule appears also to be the only exception to the rule.

3. The amount of the β-form in diisobutylene depends on the conditions of preparation. Diisobutylene prepared according to Butlerov's method contains the greatest amount of the β-form (~20%), and a considerably lower amount is obtained by splitting HCl with the aid of alcoholic alkali off 2-Cl-2,4,4-trimethylpentane (~10%) and off 2-I-2,4,4-trimethylpentane.

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ISOMERIZATION OF ALKANES IN PRESENCE OF AlCl₃ UNDER A PRESSURE OF HYDROGEN

COMMUNICATION 1. ISOMERIZATION OF n-HEXANE

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The isomerization of n-hexane in presence of aluminum chloride was first investigated by Moldavsky and coworkers [1], who established the existence of an induction period in the isomerization and also the promoting effect of HCl. In later work by Moldavsky and Nizovkina on the isomerization of pentane [2], a hexane fraction was obtained, and investigation showed this to contain a large amount of 2,2-dimethylbutane [3]. Attention must be drawn to the work of Petrov, Meshcheryakov, and Andreev [4], and also to the investigation of Moldavsky, Kobylskaya, and Livshits [5] on the isomerization of alkanes in presence of AlCl₃ under a pressure of hydrogen. In this and later work [6] it was shown that it was desirable for the isomerization of alkanes in presence of AlCl₃ to be carried out under a pressure of hydrogen in order to suppress side reactions. However, no systematic study of the effect of the value of the pressure on the direction and rate of isomerization has yet been carried out. It has been established only that replacement of hydrogen by nitrogen results in a reversion to cracking and the formation of a "lower layer". It has been established also that isomerization occurs only in presence of moisture or HCl, even in very small quantity; in some investigations equimolecular amounts of AlCl₃ and HCl were used. It is very notable that when carrying out the isomerization of n-hexane under a pressure of hydrogen (of some tens of atmospheres) the catalyst remains crystalline and its active life is considerably increased. Finally, it has recently been shown [6] that addition of cycloalkanes or of small amounts of benzene to alkanes greatly suppresses cracking. The addition of powdered aluminum to the catalyst acts in the same direction. Such are the most important features of the isomerization of n-hexane in presence of AlCl₃ that have been known up to the present time.

In the present work we have investigated the isomerization of n-hexane in presence of hydrogen at pressures of up to 1500 atm. We used commercial aluminum chloride and n-hexane that had been purified from small amounts of contaminating unsaturated and aromatic hydrocarbons by adsorption chromatography. The physical constants of the purified n-hexane were d_4^{20} 0.6594; n_D^{20} 1.3750; data in the literature [7]: d_4^{20} 0.65937; n_D^{20} 1.37486.

The boiling point of the purified hexane was 68.4-68.8° (when the hexane was distilled through a column of 30 theoretical plates, 3% distilled between 68.1 and 68.4° at 760 mm). According to data in the literature, b.p. of n-hexane is 68.74° [7].

Parallel experiments carried out under identical conditions using hexane before and after purification showed that the presence in n-hexane of small amounts of unsaturated and aromatic hydrocarbons has no appreciable effect on the rate of isomerization, when there is no cracking.

The isomerization was carried out in a shaken reactor of 150 ml capacity made of stainless steel. n-Hexane (60 g) and the calculated amount of AlCl₃ (in the form of 2-4 mm pieces) were introduced into the reactor, and hydrogen was then passed in from a cylinder under a pressure of up to 140 atm. In order to carry out experiments at greater pressures, the calculated amount of AlCl₃ was put into the reactor, hexane was added up to half the height of the reactor, hydrogen (140 atm) was passed in, and the pressure was further increased by pumping in n-hexane by means of a pump (up to 500 atm). Still greater pressures were attained by passing hexane into the reactor from a supercharged cylinder by the aid of a compressor working at super-high pressure. This procedure was adopted in order to prevent the dissolution of large amounts of compressor lubricant in hydrogen; the solubility of the lubricant in the compressed gas rises rapidly with increase in pressure.

In our experiments at pressures of greater than 140 atm, the amount of hydrogen in the reactor was about 10 liter (on reducing to 760 mm and 0°C), which ensured the saturation of hexane with dissolved gas for pressures of up to 400-500 atm (see [8]). At pressures of the order of 1000 atm and higher, the solution of hydrogen in hexane that was formed was, of course, unsaturated. After the pressure had been established, the shaken reactor was heated by means of a cylindrical electric furnace that was fixed round it. At first the pressure fell somewhat because of the dissolution of hydrogen in the hexane, but later it began to rise. The temperature of the experiment, and the corresponding pressure, was attained in 30-35 min, and it was maintained at the desired level up to the end of the experiment; after the required time, heating was discontinued and the reactor was cooled with ice.

We first carried out experiments in which n-hexane was heated with AlCl₃ under the high pressure of the liquid hexane itself, in absence of hydrogen (see Table 1). In these experiments, among the reaction products were found lower- and higher-boiling hydrocarbons (relative to the hexane fraction) and a dark-colored lower layer, the presence of which indicates that an appreciable amount of cracking occurred. After being separated, the transparent upper layer was washed with dilute NaOH solution, dried (CaCl₂), and distilled. The lower layer was decomposed by means of ice and extracted with ether; the ether layer was washed and dried, and the solvent was distilled off.

The results in Table 1 show that the isomerization of n-hexane under pressure in absence of hydrogen is accompanied by an appreciable amount of cracking.

The succeeding experiments were carried out with n-hexane and AlCl₃ in presence of hydrogen, and it was found that at a sufficiently high pressure of hydrogen (and corresponding concentration of hydrogen dissolved in hexane) the formation of a lower layer was not observed. The liquid reaction products contain only a hexane fraction.[1] The external appearance of the catalyst did not alter. The clear colorless reaction product was washed and dried; it was then distilled through a fractionating column of 30 theoretical plates. This column permitted quite satisfactory separation of 2,2-dimethylbutane (b.p. 49.7°) from the other isomers: 2,3-dimethylbutane (b.p. 58.0°), 2-methylpentane (b.p. 60.3°), and 3-methylpentane (b.p. 63.3°), but it could not guarantee quantitative separation of the other isomers (Fig. 1). The total yield of isomers was judged from the amount of the total fraction of b.p. 47-66° in its relation to

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[1] When emptying the reactor, there was generally a loss of 3-5 g of product (up to 8%) on account of its retention by aluminum chloride and of the filling of the hollow manometer spring.

the amount of fractionated liquid reaction product. The results on the rate of isomerization of n-hexane under a hydrogen pressure of 75-95 atm at 100° and a wt. ratio of AlCl$_3$/n-hexane of 0.1, 0.5, and 1.0 are given in Table 2.

An examination of the results in Table 2 leads to the following conclusions:

1. Increase in the amount of catalyst greatly increases the rate of isomerization.

2. In the process of isomerization, at first a rise, and then a gradual fall in the rate of reaction is to be observed; at the very beginning of the process, the rate of isomerization is relatively low (see Expt. 6), which confirms the known fact that there is a period of induction in the reaction. The effect of pressure and temperature on the rate of isomerization of n-hexane in presence of AlCl$_3$ and hydrogen is illustrated by the results given in Table 3.
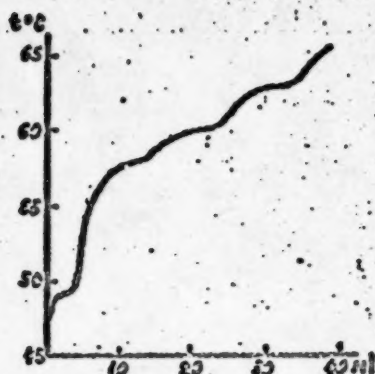
Fig. 1. Fractionation curve for hexane isomers, Expt. 7 (Table 2) at 745.7 mm (0°)
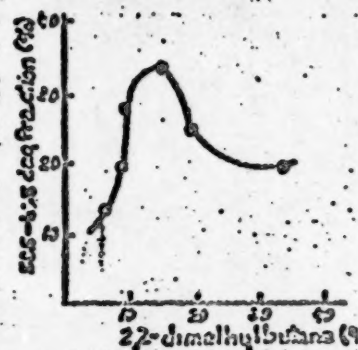
Fig. 2. Relation between the content of the 58.5-61.5° fraction and the 47-54° fraction (2,2-dimethylbutane) in the liquid reaction products (Table 5)

TABLE 3

Effect of Pressure and Temperature on the Rate of Isomerization of n-Hexane in Presence of Hydrogen

$$\left(\frac{AlCl_3}{n\text{-hexane}} = 0.5\right)$$

No.	Pressure (atm)	Tempera-ture (°C)	Time (hr)	Yield of liquid products (% of charge)	Yield of hexane isomers (fract. b.p. 47-66°) (% of liq. products)
1	85	100	7	89	58.4
2	210	100	7	86	25.0
3	430	100	6	89	8.5
4	1450	100	13	95	5.5
5	1000	80	13	94	4.5
6	1500	125	6	91	35.6

It follows from an examination of the results given in Table 3 that increase in pressure greatly reduces the rate of isomerization of n-hexane in presence of hydrogen. Increase in temperature under these conditions greatly accelerates the isomerization (at constant pressure).

Finally, we have established that addition to the n-hexane of small quantities of benzene has a significant inhibiting effect on the cracking of n-hexane in presence of AlCl$_3$ and permits a reduction in the pressure of hydrogen necessary for carrying out the isomerization. Thus an addition of 0.5% of benzene enables the isomerization of n-hexane to be carried out without appreciable cracking at 68 atm, and an addition of 10% of benzene enables it to be carried out at 35 atm. On the other hand, the rate of isomerization of n-hexane in absence of cracking is not affected appreciably by the addition of small amounts of benzene.

The behavior observed in the isomerization of n-hexane under a pressure of hydrogen is evidence that this process, in contrast to cracking, is not inhibited by small amounts of additives that may undergo alkylation. The presence of an induction period and of a maximum isomerization rate may be explained on the hypothesis that the rate of the process is determined by at least two successive reactions [9]. Finally, the reduction in the isomerization rate that we have found for increasing hydrogen pressure makes it very probable that the isomerization of n-hexane must involve the separation of hydrogen in one of its intermediate stages[1]. If such an intermediate stage occurs in the reaction, then increase in hydrogen pressure will have a delaying effect on the isomerization process for the following reasons: In the first place, it will lead to an increase in the concentration of dissolved hydrogen and so reduce the equilibrium concentration of the intermediate product. In the second place, at sufficiently high pressures the effect of pressure also as a physical factor will begin to tell on the actual value of the equilibrium constant for this intermediate stage of the reaction, which takes place with increase in volume. It should be noted that in order to determine the mechanism of the isomerization of alkanes under a high pressure of hydrogen careful study must be devoted to the part played by cracking products, the formation of which (in small quantities) cannot be altogether excluded under these conditions.

We will turn now to an examination of the composition of the mixture of isomers obtained in the present investigation. It follows from the above results that under suitable conditions the isomerization of n-hexane may proceed to an extent of greater than 80%. It was found at the same time that the content of 2,2-dimethylbutane grows considerably in the final stage of the isomerization and that there is a simultaneous fall in the content of 2-methylpentane.

In Table 4 some results are given of the fractionation (content of fractions of b.p. 47-54° and 58.5-61.5°) of liquid reaction products for all experiments in which a degree of isomerization of greater than 50% was attained. The fraction of b.p. 47-54° consists of 2,2-dimethylbutane, sufficiently well separated from the remaining isomers; the fraction of b.p. 58.5-61.5° contains mainly 2-methylpentane.

From the results in Table 4 it will be evident that the content of the 58.5-61.5° fraction passes through a clearly defined maximum at a definite 2,2-dimethylbutane content[2] (Fig. 2).

These results lead to the conclusion that the formation of 2-methylpentane forms an intermediate stage in the isomerization of n-hexane; the isomerization of 2-methylpentane evidently leads to the formation of 2,2-dimethylbutane. The part played by the remaining isomers (2,3-dimethylbutane and 3-methylpentane) and their place in the scheme of the stepwise isomerization of n-hexane demand further detailed study. In foreign literature there have recently appeared data that confirm our conclusions concerning the stepwise isomerization of n-hexane [11].

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[1] Results on the separation of small amounts of hydrogen in the initial stage of the isomerizaton of butane speak in favor of this supposition [10].

[2] A maximum, quite as definite, is shown also by the amount of the 56-61.5° fraction, which contains mainly 2-methylpentane and 2,3-dimethylbutane.

TABLE 4

Yield of Isomerization Products
(% on Weight o. Liquid Reaction Products)

No.	Fraction of b.p. 47-66°	Including	
		Fract. 47-54°	Fract. 58.5-61.5°
1	54.0	6.0	12.9
2	68.6	8.5	19.4
3	68.7	8.7	19.6
4	75.3	9.2	28.1
5	93.0	14.8	23.8
6	80.1	18.5	25.0
7	>91.0	31.5	19.2

SUMMARY

1. It has been confirmed that by carrying out the isomerization of n-hexane in presence of $AlCl_3$ under a high pressure of hydrogen cracking is reduced to a minimum and the formation of the so-called "lower layer" in the reaction products is completely avoided.

2. It has been established that increase in the hydrogen pressure reduces the rate of isomerization of n-hexane.

3. It has been established that the isomerization of n-hexane has a stepwise character; thus 2-methylpentane evidently forms an intermediate product in the formation of 2,2-dimethylbutane.

4. Some general suggestions have been made concerning the mechanism of the isomerization of n-hexane in presence of $AlCl_3$ under a pressure of hydrogen.

Draftsman-designer Opekunov and mechanic Kuznetsov took part in the work.

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KINETICS OF THE DEHYDRATION OF ALCOHOLS

IN PRESENCE OF TRICALCIUM PHOSPHATE

L. Kh. Freydlin and A. M. Levit

Among the most active and specific catalysts for the dehydration of alcohols are the oxides of aluminum [1], tungsten [2], and thorium [3]. In chemical practice, aluminum oxide has received particularly wide application. Very little investigation and practically no application have been received by the readily available and easily prepared phosphate catalysts. Thus there are only some brief indications in the literature of the dehydrating action of tricalcium phosphate. Allardyce [4] investigated the dehydration of isopropyl alcohol and Schwabb that of ethyl alcohol over calcium triphosphate [5]. We have used calcium triphosphate with success as a catalyst for the dehydration of formic acid [6].

The present work is devoted to a study of the kinetics of the dehydration of a number of alcohols, viz. ethyl, n-propyl, n-butyl, isopropyl, and isobutyl, in the presence of the same catalyst. The results that we have obtained show that tricalcium phosphate is a very active and specific catalyst for the dehydration of alcohols.

In investigating the effect of molecular weight, the position of the OH group in the alcohol molecule, and the structure of the hydrocarbon radical on the kinetics of the reaction we found that the order followed by the dehydration rates of various alcohols on a phosphate catalyst is the same as that followed on aluminum oxide in the investigations of Bork and Tolstopyatova [7]. The most readily dehydrated are isopropyl and isobutyl alcohol, and then follow the normal alcohols: n-butyl, n-propyl, and ethyl alcohol. The dehydration rate of a normal alcohol is the greater, the higher its molecular weight (see Table 8 and Figure 8). We have calculated the apparent activation energy Q for the dehydration reaction of alcohols; the values obtained are: ethyl 40,600 cal/mole, n-propyl 38,600, isopropyl 37,800, n-butyl 55,000, and isobutyl 68,000 cal/mole. This shows that on replacing an α-hydrogen of ethyl alcohol by a CH_3 group the activation energy for the reaction is lowered by 2800 cal/mole. On replacing a β-hydrogen by CH_3, the activation energy is lowered by 2000 cal/mole. An analogous phenomenon was observed by Dohse [8], Adadyrov [2], and Bork [7] in the dehydration of alcohols over other catalysts. As regards the introduction of CH_3 in the γ-position, our results for the butyl alcohols show an anomaly here: in presence of a phosphate catalyst, the activation energy for the reaction is not lowered, but raised. It is possible that the side-reaction of polymerization, the products of which were, in fact, found in the catalyzates of these alcohols, has an effect here.

The values of the pre-exponential factor (K_0) for ethyl, n-propyl, and isopropyl alcohols are close together: 4×10^{15}, 5×10^{15}, and 4×10^{16}, whereas for the butyl alcohols they attain the values: 3×10^{21} and 5×10^{24}.

As we have previously pointed out [6], dehydration catalysts usually contain chemically bound water, which they retain firmly. When subjected to thermal treatment, they are almost completely deactivated. Tricalcium phosphate also contains chemically bound water, which it retains firmly even at 500-600°. When tricalcium phosphate is calcined, its activity is greatly reduced. The view that we have previously advanced [9], according to which the active centers of the catalyst are to be regarded as OH groups containing a mobile hydrogen atom, is confirmed in our experiments with calcium phosphate and silica gel. We have established that the addition to them of potassium carbonate does in fact deactivate them for the alcohol-dehydration reaction.

A comparison of the rates of dehydration of ethyl alcohol and of diethyl ether shows that diethyl ether is not an essential intermediate product for the formation of ethylene from alcohol in presence of tricalcium phosphate.

Rollet [10] recommends silica gel as a catalyst in the preparation of unsaturated hydrocarbons from the lower alcohols. We made an attempt to study the kinetics of the dehydration of alcohols over silica gel. It was found that the catalyst was rapidly poisoned, an effect evidently associated with the formation of polymer film on the surface of the catalyst. We were successful in studying the kinetics of the dehydration only in the case of ethyl alcohol in the range 352-392°. The activation energy of the reaction is 22,500 cal/mole, i.e. twice as low as on phosphate. The value of K_O is also considerably lower, being 1.3×10^9.

EXPERIMENTAL

Experimental Conditions

The apparatus and experimental procedure have already been described [11]. The alcohol was introduced into the reaction tube at the rate of 0.16 ml/min. Tricalcium phosphate was prepared from calcium chloride and ammonium phosphate. The volume of the catalyst was 20 ml, and its weight was 9 g. In all the figures given in this paper, the relation between the degree of conversion and the temperature is shown on the left, and the conformity with the Arrhenius equation is shown on the right.

Kinetics of the Dehydration of Ethyl Alcohol

As will be seen from Table 1 and Figure 1, the degree of conversion of ethyl alcohol in presence of tricalcium phosphate rises from 3.2 to 48.4% when the temperature rises from 333 to 387°. The gas obtained contains 98-99% of ethylene. $Q = 40,600$ cal/mole; $K_O = 4 \cdot 10^{15}$. The catalyst is stable; it retains its activity unchanged over the course of many hours.
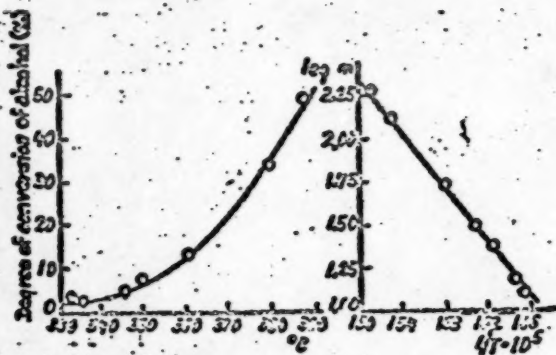
Kinetics of the Dehydration of n-Propyl Alcohol

It will be seen from Table 2 and Figure 2, that when the temperature was increased from 322 to 356°, the degree of conversion of the alcohol rose from 8.2 to 46.4%. The propene content of the gas was 99%. $Q = 38,600$ cal/mole, $K_O = 5 \cdot 10^{15}$. The activity of the catalyst was checked systematically over 5 hours, and no change was detected. When the tricalcium phosphate was treated with potassium carbonate (5%), the degree of the conversion of the propyl

Fig. 1

alcohol at 356° was only 3%, whereas for the catalyst that did not contain potash 47% of alcohol was dehydrated under these conditions. Hence the activity of the catalyst was reduced 15 times by the addition of potash.

TABLE 1

Kinetics of the Dehydration of Ethyl Alcohol in Presence of Calcined Tricalcium Phosphate
Ethylene content in gas 98-99%; $Q = 40,600$ cal/mole; $K_O = 4 \cdot 10^{15}$

Temp. of experiment (°C)	Gas liberated per 1 ml of alcohol (ml)	Degree of conversion of the alcohol(%)
333	12.2	3.2
335	13.8	3.6
345	22.0	5.7
348	30.0	7.8
360	53.0	13.8
379	132.0	34.3
387	186.0	48.4

TABLE 2

Kinetics of the Dehydration of n-Propyl Alcohol in the Presence of Calcined Tricalcium Phosphate
Propene content in gas 99%; $Q = 38,600$ cal/mole; $K_O = 5 \cdot 10^{15}$

Temp. of experiment (°C)	Gas liberated per 1 ml of alcohol (ml)	Degree of conversion of the alcohol(%)
322	24.5	8.2
335	47.5	15.8
347	90.6	30.2
356	139.1	46.4

Kinetics of the Dehydration of Isopropyl Alcohol

As will be seen from Table 3 and Figure 3, when the temperature was increased from 262 to 297°, the degree of conversion of the alcohol rose from 6.1 to 61.8%. The propene content of the gas was 99%. $Q = 37,800$ cal/mole; $K_O = 4 \cdot 10^{16}$. It will be seen from Table 3 that the dehydration of the secondary alcohol occurs at considerably lower temperatures than that of the primary alcohols. After the catalyst had been calcined at 850° for 4 hours, its

Fig. 2

activity was greatly reduced, and the yield of propene at 296° fell from 61.4% to 1.7%, i.e. to 36 times less. The activity of the catalyst with respect to the reaction of dehydration of formic acid under analogous conditions suffered only a two-fold reduction.
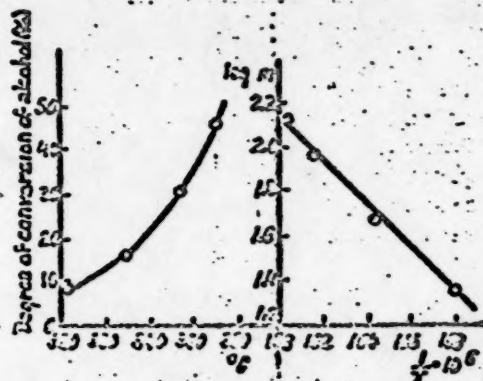
Kinetics of the Dehydration of n-Butyl Alcohol

It follows from Table 4 and Figure 4 that with increase in temperature from 319 to 353° dehydration of the alcohol increased from 6 to 69%. The butene content of the gas was 99%. $Q = 55,000$ cal/mole, $K_O = 3 \cdot 10^{21}$. Comparison of these kinetic functions with those for ethyl and propyl alcohols reveals a great increase in the values of $\underline{Q}$ and $\underline{K_O}$. It was not found possible to increase the degree of conversion of n-butyl alcohol to higher than 81% by increase in temperature.

TABLE 5

Kinetics of the Dehydration of Isopropyl Alcohol in Presence of Calcined Tricalcium Phosphate

Propene content in gas 99%; Q = 37,800 cal/mole; $K_0 = 4 \cdot 10^{16}$.

Temp. of experiment (°C)	Gas liberated per 1 ml of alcohol (ml)	Degree of conversion of alcohol (%)
262	18.0	6.1
268	30.6	10.4
272	38.1	13.0
288	108.8	37.1
292	128.1	43.4
294	141.9	48.4
297	181.2	61.8

TABLE 4

Kinetics of the Dehydration of n-Butyl Alcohol in the Presence of Calcined Tricalcium Phosphate

Butene content in gas 99%; Q = 55,000 cal/mole; $K_0 = 3 \cdot 10^{21}$.

Temp. of experiment (°C)	Gas liberated per 1 ml of alcohol (ml)	Degree of conversion of the alcohol (%)
319	14.4	6.0
332	41.6	17.2
343	99.0	40.9
351	155.2	64.1
353	168.0	69.0

Kinetics of the Dehydration of Isobutyl Alcohol

It will be seen from Table 5 and Figure 5 that with increase in temperature from 312 to 334° the degree of dehydration of the alcohol rose from 12 to 80%. The content in the gas of butenes was 99%. Q = 68,000 cal/mole; $K_0 = 5 \cdot 10^{24}$. Here, as also in the dehydration of n-butyl alcohol, a great increase in the values of Q and K_0 is to be observed. It was not found possible to increase the degree of dehydration of isobutyl alcohol to higher than 80% by increase in temperature.

Effect of the Calcination of the Phosphate Catalyst on the Kinetics of the Dehydration of Ethyl Alcohol

It follows from Table 6 and Figure 6 that after calcination of the catalyst at 600-700° for 1 hour its activity is reduced about fivefold. Hence, in order to determine the kinetics, it was necessary to carry out the reaction in the higher-temperature range. In spite of the great diminution in activity, the energy of activation for the process suffered little change.

Fig. 3

Fig. 4

When investigating the dehydration of various alcohols and their corresponding ethers on aluminum oxide over the temperature range 280-440°, Adkins and Perkins [12] concluded that dibutyl ether is not an essential intermediate product
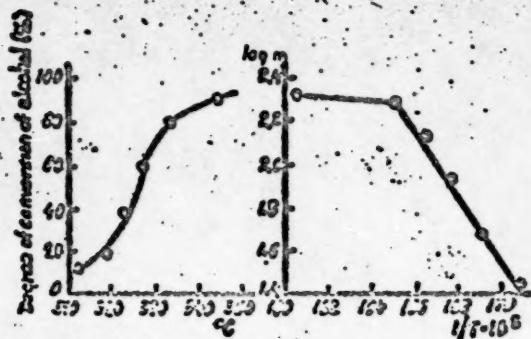
Fig. 5
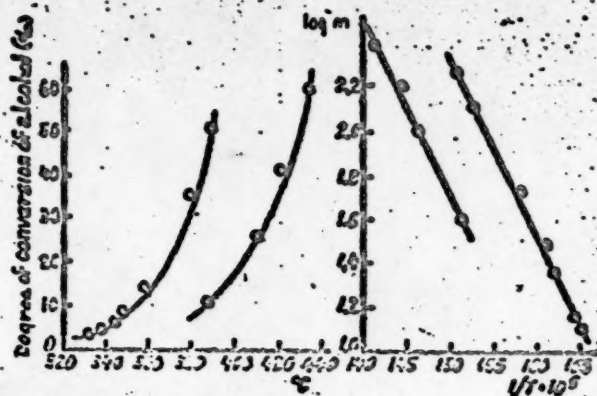
Fig. 6

in the formation of butene because it is dehydrated considerably more slowly than butyl alcohol. The rate of dehydration of diethyl ether was found to be equal to the rate of dehydration of ethyl alcohol. On the other hand, it was shown by Bischoff and Adkins [13] that on TiO_2 ethyl alcohol is dehydrated more rapidly than ether.

TABLE 5

Kinetics of the Dehydration of Isobutyl Alcohol in the Presence of Calcined Tricalcium Phosphate

Butene content in gas 99%; $Q = $ 68,000 cal/mole; $K_0 = 5 \cdot 10^{24}$.

Temp. of experiment (°C)	Gas liberated per 1 ml of alcohol (ml)	Degree of conversion of alcohol (%)
312	28.7	11.9
318	47.0	19.4
323	88.3	36.5
327	141.0	58.3
334	194.4	80.2

TABLE 6

Kinetics of the Dehydration of Ethyl Alcohol in Presence of Calcined Tricalcium Phosphate

$Q = 36,000$ cal/mole; $K_0 = 5 \cdot 10^{13}$.

Temp. of experiment (°C)	Gas liberated per 1 ml of alcohol (ml)	Degree of conversion of the alcohol (%)
388	39	10.1
410	100	26.0
420	162	42.1
434	231	60.0

In our experiments on the dehydration of ethyl alcohol on tricalcium phosphate, we found a trace of ether in the catalyzate. In order to determine whether ether is an essential intermediate product in the formation of ethylene from alcohol, we studied the kinetics of the dehydration of ethyl alcohol and of diethyl

TABLE 7

Kinetics of the Dehydration of Ethyl Alcohol and of Diethyl Ether in Presence of Calcined Tricalcium Phosphate

Substance undergoing dehydration	Temp. of experiment (°C)	Gas liberated per ml of liquid (ml)	Degree of conversion (%)	Activation energy (cal/mole)	K_0
Ethyl alcohol	326	23.0	6.0	38,300	$2 \cdot 10^{15}$
	333	32.1	8.3		
	351	83.0	21.5		
	377	278.2	72.2		
Diethyl ether	333	17.3	4.0	34,500	$5 \cdot 10^{13}$
	348	37.4	8.7		
	351	41.7	9.7		
	367	85.2	19.7		
	377	125.0	29.0		
	395	186.0	48.3		

TABLE 8

Kinetics of the Dehydration of Alcohols in Presence of Calcined Tricalcium Phosphate

Name of alcohol	Investigated temp. range (°C)	Content of unsaturated substances in gas (%)	Activation energy Q (cal/mole)	Change in the value of Q[1] (cal/mole)	K_0	Change in log K_0[1]
Ethyl	333–387	98–99	40,600	—	$4 \cdot 10^{15}$	—
n-Propyl	322–356	99	38,600	−2000	$5 \cdot 10^{15}$	−
Isopropyl	262–297	99	37,800	−2800	$4 \cdot 10^{16}$	1
n-Butyl	319–353	99	55,000	+14400	$3 \cdot 10^{21}$	6
Isobutyl	312–334	99	68,000	+27400	$5 \cdot 10^{24}$	9
Ethyl, in presence of calcined $Ca_3(PO_4)_2$	388–434	−	36,000	−4600	$5 \cdot 10^{13}$	−2
Diethyl ether in presence of calcium phosphate	333–395	−	34,500	−6100	$5 \cdot 10^{13}$	−2
Ethyl alcohol in presence of silica gel . . .	352–391	93–94	22,500	−	$1.3 \cdot 10^{9}$	−

[1] with respect to the value found for ethyl alcohol.

ether when passed at the same molar velocity, 0.087 and 0.160 ml/min respectively, over the same sample of calcium phosphate. As will be seen from Table 7 and Figure 7, the rate of dehydration of diethyl ether was found to be about half that of ethyl alcohol.

For this new sample of phosphate the following kinetic data were obtained:

For alcohol: $Q = 38,300$ cal/mole; $K_0 = 2 \cdot 10^{15}$
For ether: $Q = 34,500$ cal/mole; $K_0 = 5 \cdot 10^{13}$.

The results obtained show that although in the dehydration of ethyl alcohol in presence of tricalcium phosphate some diethyl ether is formed, as well as ethylene, the ether is not an intermediate product in the formation of ethylene.

Kinetics of the Dehydration of Ethyl Alcohol in Presence of Silica Gel

Comparison of the results in Table 9 and in Table 1 shows that the activity and specificity of silica gel in the dehydration of alcohols are appreciably less than those of the phosphate catalyst. With increase in temperature from 352 to 392°, the degree of conversion of ethyl alcohol rose from 4.9 to 14.9%. The ethylene content of the gas was 93%. $Q = 22,500$ cal/mole, $K_0 = 1.3 \cdot 10^9$. Silica gel maintains its activity for a comparatively short time, and after it has been calcined at 800° for 5 hours its activity is reduced fourfold. Thus, the calcination of silica gel has a considerably greater effect on its activity in the dehydration of alcohol than in the dehydration of formic acid.
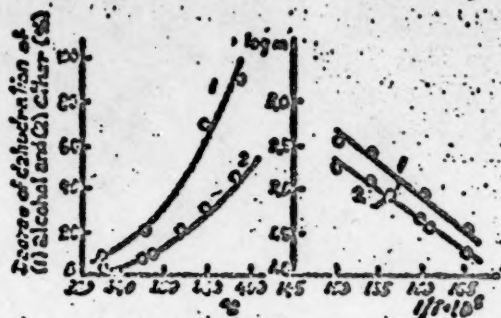
Fig. 7
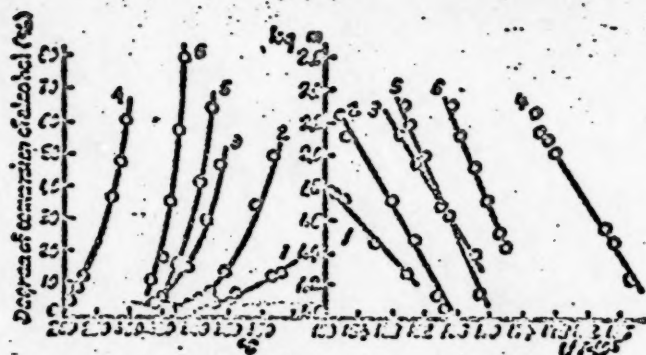
Fig. 8. Kinetic curves for the dehydration of alcohols: 1) ethyl alcohol on silica gel; 2) ethyl alcohol on phosphate; 3) n-propyl alcohol on phosphate; 4) isopropyl alcohol on phosphate; 5) n-butyl alcohol on phosphate; 6) isobutyl alcohol on phosphate.

TABLE 9

Kinetics of the Dehydration of Ethyl Alcohol in Presence of Silica Gel

Ethylene content in gas 93-94%; $Q = 22,500$ cal/mole; $K_0 = 1.3 \cdot 10^9$

Temp. of experiment (°C)	Gas liberated per 1 ml of alcohol (ml)	Degree of conversion of the alcohol (%)
352	19.0	4.9
368	30.0	7.8
390	52.6	13.9
392	57.4	14.9

SUMMARY

An investigation has been made into the kinetics of the dehydration in presence of tricalcium phosphate as catalyst of ethyl, n-propyl, isopropyl, n-butyl, and isobutyl alcohols.

1. It has been established that in presence of tricalcium phosphate the dehydration of alcohols proceeds in a very selective fashion, the content of unsaturated compounds in the gas being 98-99%

2. It has been found that in presence of tricalcium phosphate secondary alcohols are the most readily dehydrated, then follow the iso-alcohols, and

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finally the normal alcohols. The rate of dehydration of normal alcohols falls with fall in molecular weight.

3. It has been established that when the phosphate catalyst is calcined its activity in the alcohol-dehydration reaction is greatly reduced.

4. It has been shown that when an α- or β-hydrogen of ethanol is replaced by methyl the activation energy is lowered in a manner similar to that already observed for dehydration in presence of other catalysts.

5. It has been found that potassium carbonate, which is a promoter for the phosphate catalyst in the dehydration of formic acid, is a powerful poison for it in the dehydration of alcohols.

6. It has been shown that diethyl ether is not an intermediate product in the formation of ethylene from ethyl alcohol.

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THE SYNTHESIS AND REACTIONS OF VINYL ETHERS OF ETHANOLAMINES

COMMUNICATION 2. THE SYNTHESIS OF AMINOACETALS

M. F. Shostakovsky, I. A. Chekulaeva, and N. A. Gershtein

The objective of this investigation is the synthesis of aminoacetals of the following structure:

$$CH_3CH{\Large\langle}\begin{matrix}OR\\OCH_2CH_2NH_2\end{matrix}$$
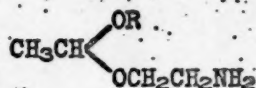
where R is an alkyl radical.

Unlike the aminoacetals that contain the amino group in the aldehyde part of the molecule $\left(NH_2-CH_2-CH{\Large\langle}\begin{matrix}OR\\OR\end{matrix}\right)$ [1,2,3,4], these compounds have received little study. In a few papers, rather complex methods for their synthesis have appeared, viz. reduction of the corresponding nitro compounds and nitriles [5,6,7]. For preparing the acetals we required, we first of all examined the simple methods developed in our laboratories of synthesizing acetals from vinyl ethers [8,9]. Two methods of synthesis were considered; they may be represented as follows:

1. $CH_2=CH-OCH_2CH_2NH_2 + ROH$

2. $CH_2=CH-OR + HOCH_2CH_2NH_2$ $\longrightarrow CH_3CH{\Large\langle}\begin{matrix}OR\\OCH_2CH_2NH_2\end{matrix}$
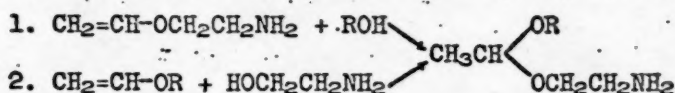
However, it was found that the presence of the amino group in the starting substances (alcohol or vinyl ether) prevents the addition of alcohols to vinyl alkyl ethers. An attempt to remove this difficulty by replacing these vinyl ethers and alcohols containing free amino groups by their salts ($CH_2=CH-OCH_2CH_2NH_2\cdot HX$ and $HOCH_2CH_2NH_2\cdot HX$, where HX = HCl and CH_3COOH) also did not yield a positive result.

The synthesis of β-aminoethyl alkyl acetals was effected by the use of the corresponding β-chlorethyl alkyl acetals, which were caused to react with liquid ammonia:

$$CH_3CH{\Large\langle}\begin{matrix}OR\\OCH_2CH_2Cl\end{matrix} + 2NH_3 \rightarrow CH_3CH{\Large\langle}\begin{matrix}OR\\OCH_2CH_2NH_2\end{matrix} + NH_4Cl.$$

$$(I)$$
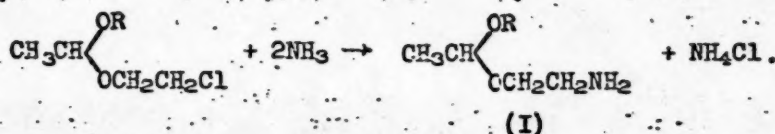
Aminoacetals containing secondary and tertiary amino groups were formed as by-products:

$$CH_3CH{\Large\langle}\begin{matrix}OR\\OCH_2CH_2NH_2\end{matrix} + CH_3CH{\Large\langle}\begin{matrix}OR\\OCH_2CH_2Cl\end{matrix} \xrightarrow{-HCl} CH_3CH{\Large\langle}\begin{matrix}OR\\OCH_2CH_2NH\cdot CH_2CH_2O\end{matrix}{\Large\rangle}\begin{matrix}RO\\\end{matrix}CH_3CH \rightarrow$$

$$(II)$$

$$+ CH_3CH \begin{array}{c} OR \\ OCH_2CH_2Cl \end{array} \xrightarrow{-HCl} CH_3CH \begin{array}{c} OR \\ OCH_2CH_2-N-CH_2CH_2O \end{array} \begin{array}{c} RO \\ CH-CH_3 \end{array}$$

(III)
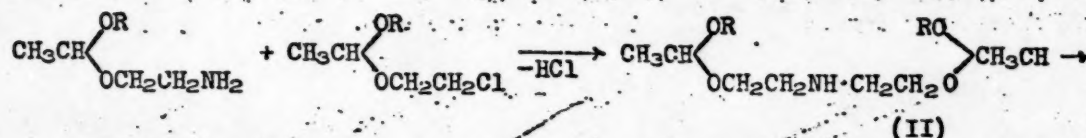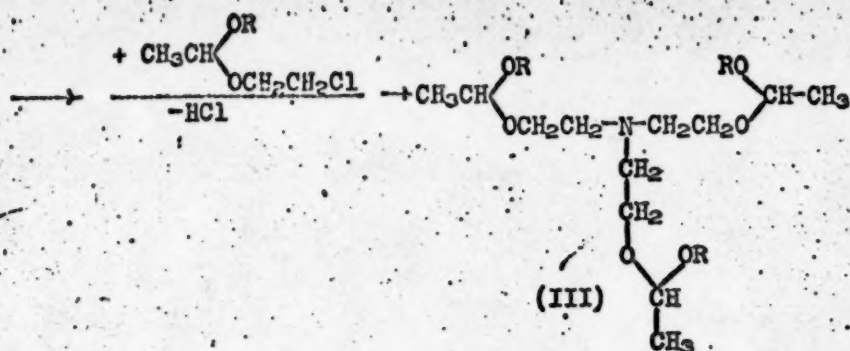
This reaction was studied in some detail, the β-chloroethyl isopropyl acetal and the β-chloroethyl isobutyl acetal of acetaldehyde being taken as examples. By variation of the reaction conditions (relative amounts of the substances, temperature, duration of reaction), the reaction may be directed so as to give mainly the β-aminoethyl alkyl acetal, or to give the products of its further reaction. The results of the experiments are given in the Table, and from this it will be seen that:

1. The reaction proceeds even at room temperature, but very slowly.

2. Even with a great excess of ammonia relative to the chloroacetal (20:1), it was not possible to obtain the β-aminoethyl alkyl acetal exclusively.

3. With reduction in the excess of ammonia relative to the chloroacetal, or with increase in the duration of the reaction for a given ratio of the starting substances, the yields of the by-products, II and III, increase.

Thus, these reactions can afford one of the simplest methods for the synthesis of aminoacetals having secondary and tertiary amino groups. It was found also that in the reaction of the chloroacetal with ammonia hydrogen chloride is not split off, and only the replacement of the halogen by the amino group occurs. This is in complete agreement with the data in the literature, from which it is evident that the splitting off of hydrogen chloride from bis(β-chloroethyl) acetals and alkyl β-chloroalkyl ethers demands fairly severe conditions (reaction with alkali at 170-300°) [14].

The aminoacetals obtained have a number of peculiarities:

1. They do not undergo disproportionation under the conditions of synthesis.

2. They are difficult to hydrolyze. Hydrolysis with 15% H_2SO_4 by heating in a closed tube on the water bath proceeds only to the extent of 80%, whereas the hydrolysis of dialkyl acetals occurs so readily that it may be used as a quantitative method for the estimation of the latter.

The peculiarities in the behavior of the aminoacetals, as also the unsuccessful attempts to prepare them from β-aminoethyl vinyl ether ($CH_2=CH-OCH_2CH_2NH_2$) and β-aminoethanol ($HOCH_2CH_2NH_2$), result from the effect of an amino group in the β-position to oxygen. The starting materials, the alkyl β-chloroethyl acetals, have also an interest of their own. In the literature, only β-chloroethyl ethyl acetal and butyl β-chloroethyl acetal have been described; they were prepared by the interaction of alkyl vinyl ethers and β-chloroethanol [10]:

$$CH_2=CH-OR + HOCH_2CH_2Cl \longrightarrow CH_3CH \begin{array}{c} OR \\ OCH_2CH_2Cl \end{array}$$
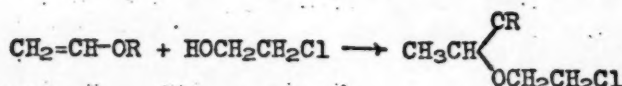
We chose the same method of synthesis. At the same time we examined the effect of a radical of iso-structure on the degree of disproportionation of mixed acetals:

$$2CH_3CH\begin{cases}OR\\OCH_2CH_2Cl\end{cases} \longrightarrow CH_3CH\begin{cases}OR\\OR\end{cases} + CH_3CH\begin{cases}OCH_2CH_2Cl\\OCH_2CH_2Cl\end{cases}$$
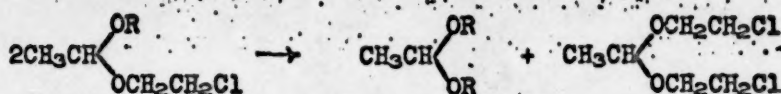
It was shown that also in this case there were formed, in addition to the alkyl β-chloroethyl acetal (yield 56-57% of theory), secondary reaction products: the dialkyl acetal (21-25%) and the bis(β-chloroethyl) acetal (37-44%). Hence, an iso-alkyl radical has no inhibiting effect on the disproportionation of mixed acetals.

TABLE

Dependence of the Yield of Aminoacetals on Reaction Conditions

Expt. No.	Molar ratio of NH_3 to Cl-acetal	Duration of reaction, hours	Temperature of reaction, (°C)	Yield on original chloroacetal, %			
				Total yield	Of aminoacetals containing the group		
					$-NH_2$	$>NH$	$>N-$
1	20:1	5-6	140-150	76.5	42.4	28.5	5.6
2	20:1	8-10	140-150	80.2	13.7	49.0	16.5
3	9:1	10	140-150	79.2	24.6	27.3	27.3
4	4:1	10	140-150	82.4	20.7	21.3	40.4
5	32:1	336	25	54.0	38.0	16.0	—

EXPERIMENTAL

I. Synthesis of β-Chloroethyl Isopropyl Acetal $CH_3CH\begin{cases}OC_3H_7\text{-iso}\\OCH_2CH_2Cl\end{cases}$

The reaction was carried out in a three-necked flask with stirrer, dropping funnel, and thermometer. The starting substances were β-chloroethanol, which was purified by distilling three times, and isopropyl vinyl ether. The isopropyl vinyl ether (b.p. 54.5-55.5°; n_D^{20} 1.3850) (123.9 g) was added dropwise under stirring during 2 hours to an equimolecular amount (112.8 g) of β-chloroethanol (b.p. 126-127°; n_D^{20} 1.4407). The reaction is an exothermic one, and the temperature rose from 15 to 45°. When the vinyl ether had been added, the mixture was allowed to stand for 10-12 hours. The reaction products were fractionally distilled several times at atmospheric and at reduced pressure. The following fractions were obtained:

Fraction I, b.p. 103-122° at 760 mm — 2.5 g;
Fraction II, b.p. 123-130° at 760 mm — 30.7 g;
Fraction III, b.p. 35-72° at 22 mm — 5.2 g;
Fraction IV, b.p. 75-79° at 26 mm — 138.8 g;
Fraction V, b.p. 80-100° at 26 mm — 1.0 g;
Fraction VI, b.p. 125-128° at 40 mm — 55.7 g;
_____
239.9 g.

By vacuum distillation of Fraction IV, a product (135 g = 56.3% of theory) was isolated, which corresponded according to its analysis to β-chloroethyl isopropyl acetal: b.p. 58-61° at 10 mm;[1] n_D^{20} 1.4192; d_4^{20} 0.9865; MR_D 42.66; calculated for $C_7H_{15}O_2Cl$: MR_D 42.67; M (determined cryoscopically in benzene) 166.45; 168.2; calculated for $C_7H_{15}O_2Cl$ M 166.6.

_____
[1] Most of the acetals have the property of boiling over a range of 3-5°.

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Found %: C 50.56, 50.50; H 9.07, 9.32.

$C_7H_{15}O_2Cl$. Calculated %: C 50.46;   H 9.07.

Found %: Cl 21.49, 21.25.

$C_7H_{15}O_2Cl$. Calculated %: Cl 21.29.

Hydrolysis with 2% H_2SO_4 followed by estimation of acetaldehyde by the bisulfite method:

0.2059 g substance: 24.34 ml 0.1 N I_2; % acetal 98.5.
0.1936 g substance: 22.95 ml 0.1 N I_2; % acetal 98.8.

β-Chloroethyl isopropyl acetal is a colorless mobile liquid with a pleasant odor, soluble in ether, benzene, and alcohol.

Fraction II was treated with metallic sodium and distilled under atmospheric pressure. Diisopropyl acetal (25 g; 21.6% of theory) was isolated; b.p. 125-128° at 760 mm; d_4^{20} 0.8140; n_D^{20} 1.3885. Literature data: b.p. 125-128° d_4^{20} 0.8142; n_D^{20} 1.3882 [8].

Fraction VI was distilled under reduced pressure and yielded bis(β-chloroethyl) acetal (50 g; 37.0% of theory); b.p. 92-93° at 6 mm; n_D^{20} 1.4529; d_4^{20} 1.1803; MR_D 42.83; calculated for $C_6H_{12}O_2Cl_2$ MR_D 42.92. (Literature data: b.p. 104-105° at 10 mm; n_D^{20} 1.4529; d_4^{20} 1.1737 [10]; $n_D^{16.2}$ 1.4532; d_{19} 1.1712 [11].)

II. Synthesis of β-Chloroethyl Isobutyl Acetal $CH_3CH\begin{smallmatrix}OC_4H_9\text{-iso}\\OCH_2CH_2Cl\end{smallmatrix}$
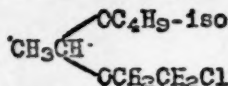
The experiment was carried out under conditions similar to those of the previous experiment. To β-chloroethanol (188.4 g) was added isobutyl vinyl ether (232 g)(b.p. 82-83°; n_D^{20} 1.3990) over a period of two hours. Vacuum distillation of the reaction products gave the following results.

Fraction   I, b.p. 60-65° at 15 mm   — 57.4 g
Fraction   II, b.p. 75-84° at 15 mm   — 240.6 g
Fraction III, b.p. 89-98° at 15 mm   — 116.8 g
Intermediate fractions   — 4.5 g
                                       419.3 g

After repeated vacuum fractionation of Fraction II a product (230.5 g, 56.2% of theory) was obtained as a colorless mobile liquid having the following constants: b.p. 74-77° at 11 mm; n_D^{20} 1.4230; d_4^{20} 0.9724; MR_D 47.30. Calculated for $C_8H_{17}O_2Cl$ MR_D 47.29; M (determined cryoscopically in benzene) 178.0, 178.5; calculated for $C_8H_{17}O_2Cl$: M 180.6.

Found %: C 53.06, 53.18; H 9.36, 9.49.

$C_8H_{17}O_2Cl$. Calculated %: C 53.18;   H 9.49.

Found %: Cl 19.64, 19.63.

$C_8H_{17}O_2Cl$. Calculated %: Cl 19.62.

Hydrolysis with 2% H_2SO_4 followed by estimation of acetaldehyde by the bisulfite method:

0.2775 g substance: 29.91 ml 0.1 N I_2; % acetal 97.3.
0.1785 g substance; 19.37 ml 0.1 N I_2; % acetal 97.9

The analytical results correspond to the required β-chloroethyl isobutyl acetal.

Fraction I was treated with metallic sodium and distilled, yielding diisobutyl acetal (50.1 g; 24.8% of theory); b.p. 55-57° at 8 mm; n_D^{20} 1.4025; d_4^{20} 0.8235; MR_D 51.51. Calculated for $C_{10}H_{22}O_2$ MR_D 51.66. (Literature data: b.p. 168-170°; d^{22} 0.816 [12,13].)

From Fraction III, bis(β-chloroethyl) acetal was isolated (97 g, 44.5% of theory); b.p. 92-93° at 6 mm; n_D^{20} 1.4529 (see previous synthesis).

III. Synthesis of β-Aminoethyl Isopropyl Acetal $\quad CH_3CH \Big\langle \begin{matrix} OC_3H_7\text{-iso} \\ OCH_2CH_2NH_2 \end{matrix}$
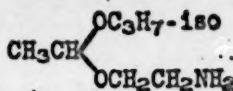
The synthesis was carried out in a stainless steel autoclave of 150 ml capacity. The starting materials were β-chloroethyl isopropyl acetal (b.p. 58-61° at 10 mm; n_D^{20} 1.4192) and ammonia. The autoclave was cooled to −50°, and β-chloroethyl isopropyl acetal (16.4 g) and liquid ammonia (50 ml = ten times the theoretical amount) were introduced. The temperature was raised to 140-150° and was maintained at this level for 6 hours. The maximum pressure was 110 atm. The autoclave was cooled to room temperature and emptied. The gas from the autoclave was released through a valve into a flask containing water (to absorb excess ammonia) and then to a gas holder filled with salt solution. Nothing collected in the gas holder, the whole of the gas being absorbed by the water. The reaction products consisted of a dark-yellow mixture of liquid and solid. These were separated by filtering on a Buchner funnel. The residue was washed with ether. The ether was distilled off, and the residue (3.1 g) from the distillation was united with the main filtrate (9.6 g); this was distilled under reduced pressure in a stream of nitrogen. The following are the results of the fractionation:

Fraction   I, b.p.   71-76° at 19 mm − 6.9 g
Fraction   II, b.p. 145-155° at 6 mm − 3.8 g
Fraction III, b.p. 180-200° at 6 mm − 1.1 g
Intermediate fractions   0.9 g
                                        _____
                                         12.7 g

Fraction I was repeatedly redistilled, and a substance (6.1 g: 37.2% on original chloroacetal) with the following constants was obtained: b.p. 75-76° at 20 mm; n_D^{20} 1.4240; d_4^{20} 0.9123; MR_D 41.18. Calculated for $C_7H_{17}O_2N$: MR_D 41.23; M (determined cryoscopically in benzene) 151.6, 151.5; calculated for $C_7H_{17}O_2N$ M 147.2.

Found %: H 11.71, 11.65; C 57.0, 56.97.
$C_7H_{17}O_2N$. Calculated %: H 11.64; $\qquad$ C 57.11.
Found %: N 9.45; 9.26.
$C_7H_{17}O_2N$. Calculated %: N 9.51.

According to these results, the product of b.p. 75-76° at 20 mm corresponds to β-aminoethyl isopropyl acetal; it is a colorless liquid with a weak ammoniacal odor, soluble in ether, benzene, alcohol, acetone, and dioxane; with a solution of sodium nitroprusside in presence of acetone it gives a violet coloration, which indicates the presence of a primary amino group.

Repeated fractionation of Fraction II in a stream of nitrogen under reduced pressure gives a second reaction product (3.0 g, 18.3% on original chloroacetal); b.p. 147-153° at 6 mm; n_D^{20} 1.4300; d_4^{20} 0.9326; MR_D 76.84; Calculated for $C_{14}H_{31}O_4N$ MR_D 77.02; M (determined cryoscopically in benzene) 283.1, 281.1; calculated for $C_{14}H_{31}O_4N$: M 277.4.

Found %: C 60.47, 60.41; H 11.26, 11.37.
$C_{14}H_{31}O_4N$. Calculated %: C 60.61; $\qquad$ H 11.26.
Found %: N 5.25, 5.12.
$C_{14}H_{31}O_4N$ Calculated %: N 5.05.

According to the analytical results, the product of b.p. 147-153° at 6 mm corresponds to the following compound:

$$\left(CH_3CH\begin{matrix} OC_3H_7\text{-iso} \\ OCH_2CH_2 \end{matrix}\right)_2 NH.$$
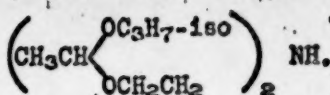
It is a pale-yellow liquid, soluble in ether, alcohol, and benzene. It gives the nitroprusside color reaction that is indicative of an amino group. The solid reaction product (4.1 g) is ammonium chloride:

<div align="center">

Found %: Cl 66.31.

NH_4Cl. Calculated %: Cl 66.36.

</div>

If the reaction conditions are altered by reducing the amount of ammonia and increasing the duration of the reaction (see Table), it is possible to increase the yield of Fraction III, from which, by vacuum distillation in a stream of nitrogen, a substance is obtained for which analysis indicates the following formula:

$$\left(CH_3CH\begin{matrix} OC_3H_7\text{-iso} \\ OCH_2CH_2 \end{matrix}\right)_3 N.$$
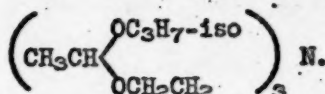
It is a yellow liquid, soluble in ether and benzene; b.p. 185-195° at 6 mm; n_D^{20} 1.4340; d_4^{20} 0.9397; MR_D 112.92; calculated for $C_{21}H_{45}O_6N$: MR_D 112.97.

<div align="center">

Found %: C 61.73, 61.88; H 11.17, 11.15.

$C_{21}H_{45}O_6N$. Calculated %: C 61.92;   H 11.05.

Found %: N 3.86, 3.72.

$C_{21}H_{45}O_6N$. Calculated %: N 3.44.

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In order to verify that the product of b.p. 185-195° at 6 mm is an individual substance, it was separated into five fractions at 2° intervals. The molecular refraction was determined for each fraction. Coincident results were obtained.

<div align="center">

IV. The Reaction of β-Chloroethyl Isobutyl Acetal with Ammonia

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The reaction was carried out in an autoclave at 140-150°, the ratio of ammonia to chloroacetal being varied (see Table). In each experiment the following aminoacetals were obtained:

1) β-Aminoethyl isobutyl acetal $CH_3CH\begin{matrix} OC_4H_9\text{-iso} \\ OCH_2CH_2NH_2. \end{matrix}$
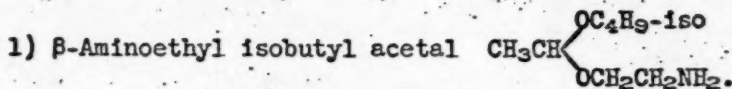
A colorless, mobile liquid having a weak ammoniacal odor, soluble in ether, benzene, and alcohol; b.p. 83-84° at 9 mm; n_D^{20} 1.4246; d_4^{20} 0.9000; MR_D 45.77. Calculated for $C_8H_{19}O_2N$: MR_D 45.85; M (determined cryoscopically in benzene) 158.1, 155.5; calculated for $C_8H_{19}O_2N$: M 161.2.

<div align="center">

Found %: C 59.33, 59.17; H 11.93, 11.95.

$C_8H_{19}O_2N$. Calculated %: C 59.60;   H 11.87.

Found %: N 8.36, 8.23.

$C_8H_{19}O_2N$. Calculated %: N 8.69.

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2) Bis-(α-isobutoxyethyl) ether of diethanolamine

<div align="center">

$CH_3CH\begin{matrix} OC_4H_9\text{-iso} \\ OCH_2CH_2 \end{matrix}$ —N— $\begin{matrix} iso\text{-}H_9C_4O \\ CH_2CH_2O \end{matrix}CH\text{-}CH_3$

|
H

</div>
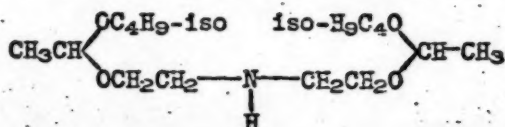
A yellow liquid, soluble in ether and benzene; b.p. 160-165° at 4 mm; n_D^{20} 1.4320; d_4^{20} 0.921; MR_D 85.97; calculated for $C_{16}H_{35}O_4N$: MR_D 86.25.

M (determined cryoscopically in benzene) 304.5, 299.6; calculated for $C_{16}H_{35}O_4N$: M 305.4.

Found %: C 63.04, 62.91; H 11.55, 11.35.
$C_{16}H_{35}O_4N$. Calculated %: C 62.91; H 11.55.
Found %: N 4.76, 4.84.
$C_{16}H_{35}O_4N$. Calculated %: N 4.58.

3) Tris(α-isobutylethyl) ether of triethanolamine
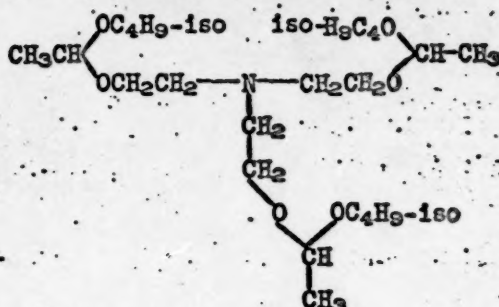
A yellow liquid, soluble in ether and benzene. B.p. 210-220° at 4 mm; n_D^{20} 1.4380; d_4^{20} 0.9322; MR_D 126.6; calculated for $C_{24}H_{51}O_6N$: MR_D 126.8.

Found %: C 63.81, 63.72; H 11.40, 11.41.
$C_{24}H_{51}O_6N$. Calculated %: C 64.10; H 11.43.
Found %: N 3.43, 3.45.
$C_{24}H_{51}O_6N$. Calculated %: N 3.11.

The individuality of the product was proved by separating it into narrower fractions and determining the molecular refraction on each of these.

SUMMARY

1. β-Chloroethyl isopropyl acetal and β-chloroethyl isobutyl acetal have been prepared.

2. It has been shown that a radical of iso-structure does not inhibit the disproportionation of mixed chloroacetals.

3. β-Aminoethyl isopropyl acetal and β-aminoethyl isobutyl acetal and also aminoacetals containing secondary and tertiary amino groups have been synthesized.

4. It has been established that the yields of aminoacetals containing primary, secondary, and tertiary amino groups depend on the reaction conditions.

5. It has been found that, unlike dialkyl acetals, aminoacetals are difficult to hydrolyze and do not undergo disproportionation under the conditions of synthesis.

6. The peculiar properties of aminoacetals are to be explained by the presence in their molecules of an amino group in the β-position to oxygen.

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MACROMOLECULAR COMPOUNDS

COMMUNICATION 43. SIGNIFICANCE OF ACIDOLYSIS IN THE POLYESTERIFICATION REACTION

V. V. Korshak and S. V. Vinogradova

In one of our previous communications [1] we investigated the kinetics of the acidolysis of ethyl stearate by acetic acid and showed that this ester reacts readily with acetic acid; at 250°, equilibrium is established at 44% conversion. It was interesting to elucidate the role of acidolysis in the case of dicarboxylic acids, since these are the initial materials for the preparation of polyesters. The ability of polyesters to undergo acidolysis with dicarboxylic acids was established long ago [2]. However, from the point of view of kinetics, this process has not been investigated. In order to study the acidolysis reaction, we investigated the kinetics of a model reaction, viz. ethyl stearate with succinic acid and also ethyl stearate with adipic acid.

Menshutkin [3] has shown that the process of esterifying polybasic acids is quite similar to that of esterifying monobasic acids, and the change in reaction rate in accordance with structure goes in the same direction as for monobasic acids: primary acids give the highest rate, tertiary – the lowest. According to the data available in the literature on the alcoholysis [4] and transesterification of monobasic acids [5], it may be concluded that also in the case of the transesterification of dicarboxylic acids, these laws still hold. There are few data in the literature on the reaction of acidolysis by dicarboxylic acids [6], and the kinetics of this process have, in general, not been investigated; hence, such an investigation has also a special interest of its own. The present work has for its objective the investigation of the course of the acidolysis by dicarboxylic acids with time at various temperatures, the elucidation of the effect of the ratio of the initial components on the result of transesterification, and also the determination of the effect that sulfuric acid has on the acidolysis reaction, for in the literature there are indications that sulfuric acid catalyzes the acidolysis process considerably less effectively than it does the processes of alcoholysis or simple esterification [7].

Initial Materials

The ethyl stearate employed was prepared by us by heating ethyl alcohol and stearic acid in presence of sulfuric acid as catalyst. The ester had m.p. 33° (literature data 33.7° [8]) and ester value 182 (calculated 179.5). The succinic and adipic acids were recrystallized from water and had acid values agreeing with those calculated.

Experimental Procedure

In the experiments on acidolysis by dicarboxylic acids, the procedure already applied in the investigation of the acidolysis of ethyl stearate by acetic acid [1] was employed.

Analytical Procedure

The procedure used for the analysis of the products of the acidolysis of

ethyl stearate by succinic and adipic acids, in accordance with the equation

$$2C_{17}H_{35}COOC_2H_5 + HOOC(CH_2)_n \cdot COOH \rightleftarrows 2C_{17}H_{35}COOH + C_2H_5 \cdot OOC(CH_2)_nCOOC_2H_5$$
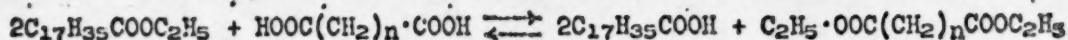
was based on the fact that the stearic acid that is formed during the reaction is insoluble in water, and it is therefore possible to make a quantitative determination of succinic or adipic acid, which is soluble in water. Thus, at 20°, the solubilities in water are: succinic acid, 5.8%; adipic acid, 1.6%, [9]. The solubilities in water of these acids may be increased by increasing the temperature.

The analysis was carried out as follows: the contents of the tube were dissolved in 100 ml of distilled water at 50-60°. After allowing to stand for 10-15 minutes with occasional shaking, the contents of the flask were cooled to room temperature. The precipitate was filtered off, and the filtrate was titrated with 0.1 N NaOH in presence of phenolphthalein. In order to verify the accuracy of the method, mixtures of equivalent amounts were taken: 1) 1 mole of adipic acid to 2 moles of ethyl stearate; 2) 1 mole of succinic acid to 2 moles of ethyl stearate. Each mixture was melted up, dissolved in distilled water, warmed to 50°, and filtered off from the residue. The filtrate was titrated with 0.1 N NaOH. Experiment showed that adipic and succinic acids titrate quantitatively in presence of phenolphthalein.

EXPERIMENTAL

a) Acidolysis of Ethyl Stearate with Succinic Acid

1. The acidolysis of ethyl stearate with succinic acid was carried out at three different temperatures: 122-123°; 168-169°; 183-184°. Ethyl stearate and succinic acid were taken in the molar ratio of 2:1. The results of the experiments are given in Table 1.

TABLE 1

Tube No.	Amount of succinic acid that has reacted, %	Duration of heating, hours	Temperature, °C	Tube No.	Amount of succinic acid that has reacted, %	Duration of heating, hours	Temperature, °C
1	3.4	1	122-123	4	14.3	4	168-169
2	4.3	2	122-123	5	15.8	5	168-169
3	5.5	3	122-123	6	16.0	6	168-169
4	11.4	4	122-123				
5	11.6	5	122-123	1	11.9	1	183-184
				2	18.9	2	183-184
1	9.2	1	168-169	3	20.9	3	183-184
2	12.6	2	168-169	4	21.9	4	183-184
3	12.6	3	168-169				

2. The effect of various ester-acid ratios on the acidolysis of ethyl stearate by succinic acid was then investigated. The tubes were heated for 5 hours at 168-169°. The results of the experiments are given in Table 2.

3. The acidolysis of ethyl stearate by succinic acid in molar ratio 2:1 in presence of sulfuric acid (1% on weight of ethyl stearate) was then investigated. The results of the experiments are given in Table 3.

b) Acidolysis of Ethyl Stearate with Adipic Acid

The acidolysis of ethyl stearate with adipic acid was carried out at four different temperatures: 122-123°; 168-169°; 183-184°; and 250°. For the

TABLE 2

Tube No.	Amount of succinic acid that has reacted, %	Molar ratio ester:acid
1	8.2	1:1
1[1]	7.7	1:1
2	9.6	1:0.75
2[1]	11.3	1:0.75
3	15.9	1:0.5
3[1]	15.9	1:0.5
4	21.4	1:0.25
4[1]	21.2	1:0.25
5	23.2	1:0.1
5[1]	24.1	1:0.1

TABLE 3

Tube No.	Amount of succinic acid that has reacted, %	Duration of heating, hours
1	51.4	1
2	51.8	2
3	52.6	4
4	54.3	5

first three temperatures, the experiments were carried out by the method indicated above. For 250°, the tubes were heated in the vapor of boiling diphenyl[1]). The results of the experiments are given in Table 4.

TABLE 4

Tube No.	Amount of adipic acid that has reacted, %	Duration of heating, hours	Temperature, °C	Tube No.	Amount of adipic acid that has reacted, %	Duration of heating, hours	Temperature, °C
1	7.6	1	122-123	1	14.4	1	183-184
2	11.7	3	122-123	2	16.4	2	183-184
3	13.2	4	122-123	3	19.6	3	183-184
4	13.9	5	122-123	4	23.5	4	183-184
				5	23.6	5	183-184
1	13.3	1	168-169	1	16.9	1	250
2	18.7	3	168-169	2	18	2	250
3	19.5	4	168-169	3	23.4	3	250
4	22.4	5	168-169	4	27.8	4	250
				5	32	5	250
				6	32.4	6	250

DISCUSSION OF RESULTS

The results that we have obtained are shown graphically in Fig. 1, for the acidolysis by succinic acid (Tables 1 and 3), and in Fig. 2 for various amounts of succinic acid. On Fig. 3, the results are shown for acidolysis by adipic acid. From these figures it will be seen that both for succinic acid and for adipic acid the reaction rate increases with temperature. Thus, while the amount of succinic acid reacting at 122-123° is 11.6%, at 183-184° it attains 21.9%; for adipic acid: 13.9% at 122-123° rises to 23.6% at 183-184°, and to 32% at 250°.

Menshutkin has found that the rate of the esterification reaction falls with increase in the molecular weight of the acid. For the transesterification of ethyl stearate by adipic and succinic acids it would be expected that this rule would continue to hold, for a similar rule with respect to alcohols is maintained in the case of alcoholysis [3]. However, it will be seen from the curves that the reaction rate for adipic acid at 122-123° and 168-169° is higher than for succinic acid. This may be explained, evidently, by the fact that

[1]) The Russian word used here is "dinyl", evidently a typographical error. CB.
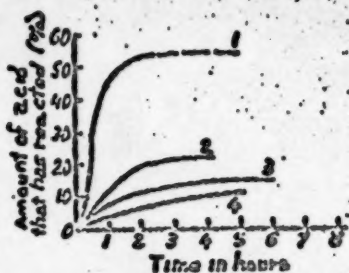
Fig. 1. 1) $\underline{t}$ 168-169°, catalyst H_2SO_4; 2) $\underline{t}$ 183-184°; 3) $\underline{t}$ 168-169°; 4) $\underline{t}$ 122-123°
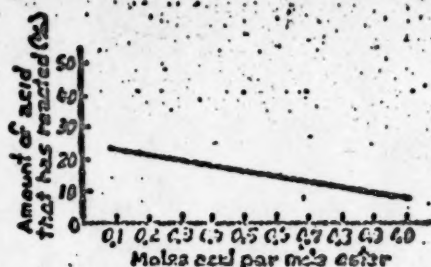
Fig. 2

succinic acid has a melting point of 183° and is in the solid state at the temperature of the reaction (succinic acid is insoluble in the ester at 183°), whereas adipic acid, which has a melting point of 153°, is soluble in the ester, and the reaction proceeds not in a heterogeneous medium, as in the case of succinic acid, but in a homogeneous one. At 183-184°, the rate of transesterification is higher in the first few hours for adipic acid than for succinic acid, but later, the rate for succinic acid becomes the higher.

TABLE 5

Temperature, °C	K	k_1 (1/g-hr.)	k_2 (1/g-hr.)	$k_1 - k_2$	m_1	m_2
250	4.32	0.222	0.956	−0.733	−0.927	0.325
183	10.4	0.111	1.15	−1.03	−0.45	0.345
168	12	0.109	1.32	−1.21	−0.387	0.314
122	38.5	0.071	2.74	−2.66	−0.194	0.165

TABLE 6

Temperature interval, °C	A_1 (cal.)	A_2 (cal.)
250-183	5540	−1490
183-168	263	−3940
168-122	3240	−5830
250-122	3870	−3490
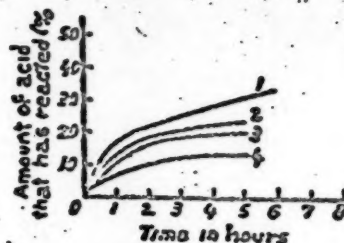
Fig. 3 1) $\underline{t}$ 250°; 2) $\underline{t}$ 183-184°; 3) $\underline{t}$ 168-169°; 4) $\underline{t}$ 122-123°

The acidolysis of the dicarboxylic acids was carried out without catalyst, and the fact that the reaction did go shows that acidolysis without catalyst is possible. It is evident that the acid itself is able in some measure to catalyze this process. In the literature there are indications [6] that sulfuric acid is not a good catalyst for acidolysis. In carrying out the acidolysis by succinic acid, an experiment was done with the objective of determining the catalytical action of sulfuric acid on the acidolysis reaction. From the curve in Fig. 1 it will be seen that sulfuric acid catalyzes the process fairly strongly.

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Whereas at 168-169° without catalyst acidolysis proceeded only to the extent of 16%, in presence of sulfuric acid (1% on wt. of ethyl stearate), it proceeded to the extent of 53%, i.e. 3.3 times more rapidly. For the acidolysis of ethyl stearate by succinic acid, the effect on the reaction of the molar proportions of ester and acid was investigated (Fig. 2). It was found that with increase in the ethyl stearate:succinic acid ratio the percent acid that reacts increases.

On the basis of the results obtained (Table 4) the equilibrium constants were calculated; also the rate constants for the forward and reverse reactions (Table 5).

The data in Table 5 served for the calculation of the activation energies of the forward and reverse process, and these are given in Table 6.

The results obtained show that part (in the case of adipic acid at 250° - 32%) of the ester taken undergoes the acidolysis reaction, and in presence of catalyst as much as half of the ester reacts. From this it may be regarded as beyond doubt that also in the process of polyesterification this process of interaction between the growing molecules and the original molecule must play, together with alcoholysis, a considerable part and will determine the limiting molecular weight and molecular weight distribution in the polymers.

SUMMARY

1. The kinetics of the acidolysis reaction of ethyl stearate with succinic and adipic acids have been investigated at 122, 168, 183, and 250°.

2. It is shown that the reaction of acidolysis by dicarboxylic acids may proceed even without a catalyst; however, sulfuric acid considerably increases the reaction rate.

3. It has been found that the molar ratio of ester and dicarboxylic acid taken has an effect on the percent conversion of the acid during acidolysis. The higher this ratio, the further the reaction goes.

4. It is shown that the acidolysis reaction is of great importance in the polyesterification process.

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CHEMICAL CHANGES PRODUCED IN THE CELLULOSE MACROMOLECULE

BY OXIDIZING AGENTS

COMMUNICATION 6. THE PRESENCE IN OXYCELLULOSES OF CARBONIC ESTER GROUPINGS AND THEIR EFFECT ON THE ESTIMATION OF URONIC CARBOXYL GROUPS

E. D. Kaverzneva, V. I. Ivanov, and A. S. Salova

In the course of our investigations into the composition of oxycelluloses, we have established that, in the determination of the uronic COOH content of oxycelluloses obtained by the action of sodium hypochlorite in acid and neutral medium, values are regularly obtained that exceed the total content of carboxyl groups in these preparations. Oxycelluloses obtained by oxidation in alkaline medium do not give this effect.

TABLE 1

Content of Total and Uronic COOH Groups in Oxycelluloses Obtained by Oxidation with NaOCl

Oxidation conditions	COOH groups equiv. to 100 gluc. res.		Difference, (1 – 2)	Oxidation conditions	COOH groups equiv. to 100 gluc. res.		Difference (1 – 2)
	By Ca acetate method (1)	Decarboxylation with 12% HCl (2)			By Ca acetate method (1)	Decarboxylation with 12% HCl (2)	
Oxidized in acid medium	0.42	0.76	−0.34	Oxidized in alkaline medium	0.38	0.43	−0.05
	0.57	1.10	−0.53		0.65	0.57	0.01
	0.74	1.04	−0.30		1.44	0.83	0.66
	2.95	3.82	−0.87		1.47	0.71	0.78
Oxidized in neutral medium	0.25	0.33	−0.08		3.49	1.58	1.91
	0.61	0.83	−0.22		4.32	3.06	1.26
	0.76	1.01	−0.95				

Similar observations were made by Kenyon and his co-workers when analyzing celluronic acids obtained by oxidation with NO_2 [1]; the cause of this phenomenon remained unknown, although these authors made a number of observations on this subject. However, behind this non-accord of two analytical methods some peculiarities in the structure of oxycelluloses that are not taken into account in the analysis may be hidden. Therefore, we considered it necessary to go into this question.

The method of determining the free COOH groups by titrating the acetic acid liberated in the reaction of the COOH groups of the oxycellulose with calcium acetate did not give us any particular reason for doubt. This method has

been frequently checked and compared with other methods of determining the acidity of cellulose [2,3]. When satisfactory elimination of mineral elements from the oxycelluloses has been achieved and when correct procedure (maintenance of pH) is used, the calcium acetate method gives good agreement with the method of reversible adsorption of methylene blue and somewhat lower results in comparison with the Ag phenate method and the method of titrating with NaOH in presence of salts.

The determination of uronic COOH groups by decarboxylation with boiling 12% HCl can under certain circumstances lead to an excessive formation of CO_2. On boiling with HCl, decarboxylation occurs not only with typical uronic acids but also, with quantitative yield, with various ketocarboxylic acids. Reaction occurs also, to an insignificant extent, with many hydroxycarboxylic acids, e.g., gluconic acid, and also glyoxalic and oxalic acids [4] and compounds not containing COOH groups [5], including glucose, which yields about 0.2% CO_2 on its weight during 5 hours of reaction. However, on carrying out the reaction on pure cotton, the amount of CO_2 evolved amounts to only 0.04% by weight. Hence, the slow formation of glucose during the hydrolysis of cellulose cannot be the cause of the enhanced evolution of CO_2 during the analysis of oxycellulose.

The separation of CO_2 from non-uronic compounds is characterized by a slow rate of reaction. While, for full decarboxylation of glucuronic acid, 3-5 hours is sufficient, the formation of CO_2 from a number of carbohydrates proceeds in regular fashion, without any abatement in ten or twenty hours [4]. Hence, the presence of non-uronic compounds that yield CO_2 on boiling with 12% HCl will have an effect on the results of prolonged experiments, but will have practically no effect on the determination of uronic acids in oxycellulose under the conditions of the 5-hour boiling given in our work.

The curves for the decarboxylation of oxycelluloses in our experiments have a fairly sharp bend at 5 hours of reaction, pointing to completion of the decarboxylation of uronic acids. Slow evolution of CO_2 continues after 5 hours; it is negligible for oxycelluloses formed in alkaline medium, but is more significant for the products of acid oxidation.

Fig. 1. Evolution of CO_2 on boiling with 12% HCl for oxycelluloses produced by acid and alkaline oxidation with hypochlorite; 1,2) pH ∼3; 3,5) pH 11; 4) pH 4,6.

It is clear that a very small amount of further decarboxylation is occurring. Calculation shows that these secondary reactions cannot cause an error of more than 0.02-0.04% in the estimation of uronic COOH in oxycelluloses, even if we introduce the corrections suggested by Whistler and others [5]. Apart from all these considerations, it is characteristic that an excessive amount of CO_2 is evolved only by those preparations formed by oxidation in acid or neutral medium. It is logical to suppose that this phenomenon is related to peculiarities in the structure of these oxycelluloses that have not been taken into account.

We have shown [6] that there are masked ester-linked carboxyls in oxycelluloses. We concluded that these blocked carboxyls form lactone linkages within the glucose residues and that such linkages should be formed most readily between the COOH at C-6 and the OH at C-3 in the glucose residues.
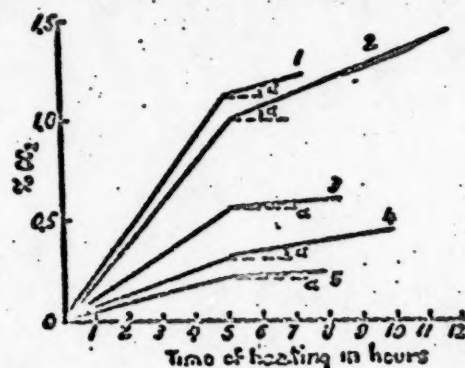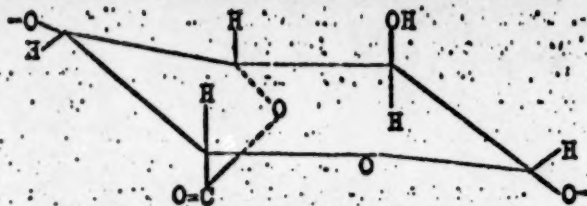
There is no doubt that such masked COOH groups will not be taken into account in methods for determining free COOH groups, but will be decarboxylated on boiling the oxycelluloses with 12% HCl and give an excessive amount of CO_2.

Thus, the most probable cause of the enhanced values, in comparison with the values for free COOH, given in the estimation of uronic COOH is the participation in the reaction of the lactonized uronic carboxyls. In order to make this conclusion quite convincing, we made a check on a number of other possible causes for the increased consumption of $Ba(OH)_2$ in the absorbers, viz.:

1) Entrainment by the passing air stream of formic acid formed during the reaction (from decomposition of carbohydrates).

2) Oxidative hydrolysis of unstable products of intermediate decomposition, with the formation of new COOH groups that undergo decarboxylation during the estimation.

3) The presence in oxycelluloses of carbonic esters that are unstable to alkalis.

As a result of our investigations, we rejected the first two of these causes and showed that it is very probable that carbonic ester groupings are present in certain oxycelluloses.

1. In experiments in which solutions of pure formic acid were boiled for 5 hours, taking amounts in excess of those that could be present when estimating uronic COOH, no appreciable carrying over of the formic acid in the air stream could be found.

The neutralization of 0.1 ml $Ba(OH)_2$, using 0.4 g of oxycellulose, gives a difference in the COOH content of 0.01%, and for a 0.2-g sample − 0.02%; these lie within the limits of the accuracy of the method.

TABLE 2

Determination of the Carry-over of Formic Acid in the Estimation of uronic COOH groups during 5 Hours of Reaction

Formic acid taken (mg)	$Ba(OH)_2$ (0.02 N) used (ml)	Formic acid carried over (mg)
1.0	0.00	0.000
2.0	0.04	0.036
2.0	0.08	0.072
30.6	0.11	0.100

2. The possibility of oxidative hydrolysis was excluded by replacing the stream of air used in the estimation of COOH groups by a stream of air-free nitrogen. This did not affect the results of the determination.

Found by analysis in stream of air (prep. No. 7) − 0.295% CO_2

Found by analysis in stream of nitrogen (prep. No. 7) $\begin{cases} - 0.290\% \ CO_2 \\ - 0.308\% \ CO_2 \end{cases}$

Consequently, oxidative processes do not cause extra evolution of CO_2 during the analysis.

3. When carbonic ester groupings are present in oxycellulose, CO_2 should split off on merely hydrolyzing with dilute alkali in the cold. In order to check on this suggestion we carried out experiments in which oxycelluloses

were hydrolyzed without access to CO_2 in the cold using CO_2-free 1% NaOH for 1 hour, followed by acidification and expelling CO_2 by blowing, also without heat. In these experiments, as in all others, parallel determinations were made on the reagents alone and, as a result, corrections for the blank were introduced. A perfectly definite result was obtained: the initial cellulose gave practically no CO_2 (Experiments 1-3), alkaline-oxidized preparations also did not react (Experiments 4-5), but the products of acid-hypochlorite oxidation gave small, but quite detectable amounts of CO_2 (Experiments 6-10).

TABLE 3

CO_2 Liberated from Oxycelluloses after Treating them with 1% NaOH in the Cold

No. of Exp.	Preparation	Amount taken (g)	CO_2 liberated (ml 0.02 N $Ba(OH)_2$	% CO_2 on amount taken	Mean % CO_2	CO_2 (equiv per 100 gluc.res.)
1	Original cellulose	1.8010	0.45	0.012		
2	Original cellulose	1.2840	0.30	0.010	0.007	0.025
3	Original cellulose	0.5160	0.00	0.00		
4	Oxycellulose, Prep.No.9	1.8560	0.05	0.010		0.018
	(alk.oxid.)	0.4610	0.05	0.001	0.005	
6	Oxycellulose, Prep. No. 7	0.5106	0.29	0.029		
7	(acid oxid.)	0.4278	0.65	0.065	0.047	0.170
8	Prep. No.1 (high degree of acid oxid.)	2.5122	2.70	0.047		
9	"	2.0130	1.80	0.039	0.044	0.160
10	"	0.5160	0.56	0.048		
11	Oxycellulose, Prep. No. 2	0.5178	0.10	0.009		
12	(neut.oxid.)	1.5940	0.89	0.024	0.016	0.060

Although the figures given in this table are very low in absolute value, they deserve to be considered, for the micro-method of determining CO_2 developed in our laboratory is distinguished by high accuracy and reproducibility, and the usual discrepancy between parallel determinations does not exceed 0.01%, as can be seen from the table.

Thus, the presence in oxycelluloses formed by acid and neutral hypochlorite oxidation of a small number of linkages of the carbonic ester type is quite probable. They can be imagined to be formed by the oxidative splitting of the pyran ring at a keto group, forming a new aldehyde or carboxyl group at C-2 and a carbonate linkage at C-1. The idea of the possible presence of carbonic ester groups was expressed by Staudinger, but it was not proved in any way [7] (see p. 203).

The amounts of carbonic esters found, however, are very small and do not account for the difference between the total and uronic carboxyl contents. Oxycellulose preparations treated with alkali in the cold and therefore not containing carbonate groups gave, nevertheless, an excess amount of uronic COOH groups.

For example, Preparation No. 7 contained:

COOH groups by the Ca acetate method . 0.74 equiv.per 100 gluc.res.
COOH groups (uronic) . . . . 1.04 equiv.per 100 gluc.res.
Carbonate groups . . . . 0.17 equiv.per 100 gluc.res.

COOH groups (uronic) after elimination
of carbonate groups . . . . 0.84 equiv.per 100 gluc.res.
(i.e., more than total COOH: . . . . . . 0.74 equiv.per 100 gluc.res.
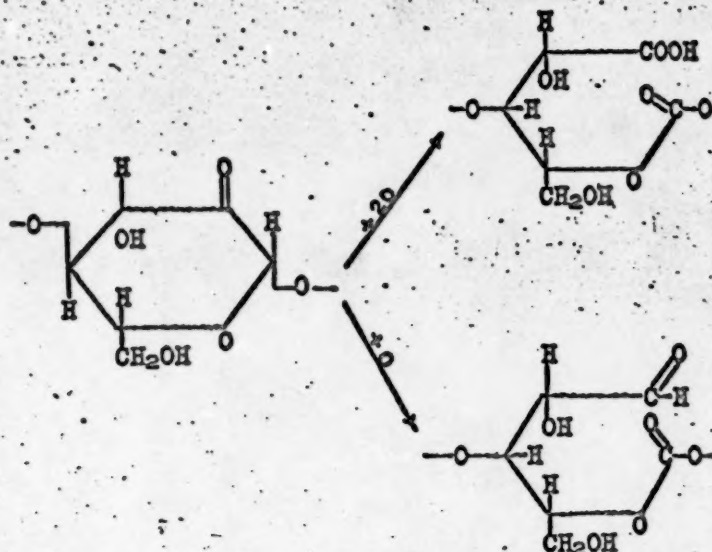
Hence, the presence of carbonate groups in oxycelluloses contributes to the increased liberation of CO_2 during decarboxylation, but is not the only cause. As the other sources that we have considered that could act in this direction have been eliminated, it must be admitted that the main cause of the increased content of uronic COOH groups in oxycelluloses, in comparison with the total free COOH groups, is the partial lactonization of the uronic COOH groups.

SUMMARY

1. The causes of the non-accord in determinations of total and uronic carboxyls in oxycelluloses prepared by the action of NaOCl in acid and neutral media have been elucidated.

2. It has been established that these causes are 1) the participation in reaction of lactonized carboxyls and 2) the presence in these oxycelluloses of a small proportion of carbonic ester groups.

3. The carbonic ester groups in oxycelluloses are very unstable, being readily hydrolysed by dilute alkali in the cold and by acids on warming. The presence of these groups is one of the contributing causes of the high instability towards alkalis of oxycelluloses formed by oxidation in an acid medium.

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DISCUSSION ARTICLES

ANSWER TO THE CRITICS OF THE NEW STRUCTURAL THEORY

G. V. Chelintsev

About three years ago I advanced the New Structural Theory [1], which was a development of the classical structural theory in the light of newly accumulated experimental data. An obstacle to the acceptance of the theory was the bitter opposition on the part of Ingold-Paulingites. Deprived of the possibility of defending the mesomerism-resonance theory in its direct form, they strive at least to cast the New Structural Theory from the threshold. While there is yet no new theory that can take the place of the mesomerism-resonance theory, they still retain the hope of preserving the latter in one or another disguised form.

Recently, a number of articles has been published criticizing the New Structural Theory. An examination of this criticism is bound to be useful. The general thesis of the critics of the New Structural Theory is that it is not in accord with "contemporary physics". Reutov writes [2]:"G.V.Chelintsev tries to construct his theory while ignoring the modern achievements of physics....". Kursanov, Gonikberg, Dubinin, Kabachnik, Kaverzneva, Prilezhaeva, Sokolov, and Freydlina write: "the understanding of the nature of the chemical bond demands the application and consideration of all the data yielded by modern chemistry and physics. One of the attempts at constructing a new theory of the chemical bond without taking these data into account is the "New Structural Theory" advanced by G.V.Chelintsev". One of the main propagandists of Pauling's resonance theory, Volkenshtein, writes [3]: "one cannot help expressing regret that in our day there should appear work devoted to matters of principle concerning the structure of chemical compounds which at the same time ignores the achievements of physical science. Such work (e.g., the work of G.V.Chelintsev) stands in sharp contradiction to the best traditions of the Russian vanguard of science, the traditions of A.M.Butlerov....", and so on.

The allegation that the New Structural Theory is invalid on physical grounds is based on two sorts of considerations. On the one hand, it is asserted that the law of the localization of orbitals on one or on two atoms, which is at the basis of the theory, is in direct contradiction to the quantum-mechanical concept of the wave properties of the electron and, consequently, the New Structural Theory has not taken into account the achievements of contemporary physics. This is simply a misunderstanding. Not in any quantum mechanics is there a postulate of the necessity of diffuseness in the electron on account of its wave properties — either throughout the universe of throughout the atoms of a particle. In quantum mechanics, atoms and molecules are regarded as highly organized systems, in which every electron has its own characteristics, and every orbital belongs to one or to two atomic nuclei. What is more, Pauli's principle directly defines the saturability of bonds, i.e., the inability of an electron to take part simultaneously in two covalent links, i.e., the impossibility of electron orbitals associated with three or more atoms. Thus, the law of the localization of

electron orbitals on one or on two atoms is in full accord with contemporary physics, and, on the contrary, the denial of this law in the concept of the delocalization of electron orbitals is nothing more than a chemical variant of the idealistic idea of free will in an electron.

The law of the localization of electron orbitals on one or on two atoms did not originate from me; it is a direct consequence of an enormous amount of chemical experience in the expression and prediction of the various types of molecule. When put in concrete form in electronic structural formulas, the law of the localization of orbitals determines the correspondence between the number of formulas and the number of actual molecules and determines the possibilities of prediction of electronic structural theory. The law of the localization of electron orbitals in one or in two atoms molds the Butlerov teaching concerning chemical structure to the pattern of electron-nucleus concepts – only in the light of this law can the qualitative differences in the interactions of chemically linked and unlinked atoms, i.e. Butlerov's assertion of the true nature of structural formulas, be understood. If in nature the law of the localization of electron orbitals did not exist, if, indeed, the wave properties of the electron predetermined that it should have a smeared character in all atoms, then the chemical world would appear not as an assembly of discrete molecules that are mutually interconvertible in stages, but as some sort of plasma of protons and electrons.

The concept of the delocalization of electron orbitals has nothing to do with contemporary scientific physics and has been devised only in mesomerism-resonance theory. The only basis for this concept is the lack of correspondence between the formulas of conjugated compounds and experimental data. This concept is nothing more than a hypothetical assumption directed towards the elimination of this non-correspondence. Why bring in quantum mechanics, contemporary physics, etc.?

On the other hand, the allegation that the New Structural Theory is invalid on physical grounds is based also on considerations concerning the non-correspondence of the theory with experimental data obtained by modern physical methods. Here it is pointed out in particular that orbit-contact formulas for benzene, ethylene, naphthalene, anthracene, etc. are in contradiction with results that indicate the absence of a center of symmetry in the benzene molecule and the absence of a dipole moment in the ethylene, naphthalene, and anthracene molecules. As it stands, this assertion can be regarded only as the result of a gross misunderstanding. Orbit-contact formulas for benzene, ethylene, naphthalene, anthracene, etc. are possible only in the light of the concept of the homopolar electrovalent bond, and the pluses and minuses in these formulas express, as stipulated, not the polarity of the bonds, but the charges of the atoms, i.e., the excess or deficiency of electrons in the electron shells of the atoms with respect to the charges on their nuclei. The assertion concerning the non-correspondence of the orbit-contact formulas of benzene, ethylene, naphthalene, anthracene, etc. with experimental data can be considered only as a not very successful attempt to assert the absurdity of the concept of the homopolar electrovalent bond.

Let us see, however, whether the concept of the homopolar electrovalent bond is quite as absurd as it appears at first glance. It is generally known that dipole moments of ionic molecules are always lower in value than would be calculated for an "ideally ionic" bond. In mesomerism-resonance theory these results are applied in considerations concerning the covalent contribu-

tion in ionic bonds, and in electronic structural theory – in considerations relating to the deformations of the electronic clouds of the atoms. From all points of view the polar state of a bond is regarded not as a result of the inflexibility (non-deformability) of the electron clouds of the atoms, but as a result of the varied electrophilic characters of the atoms.

From this it follows that in the interpretation of an electrovalent bond in terms of the law of the localization of electron orbitals there can be no objection in principle against concepts concerning the possibility of leveling out the electron density in such a bond – according to the method of the deformation of electron clouds of oppositely charged atoms (shown diagrammatically):

When the electrovalent atoms are of different electrophilic character, this leveling out is achieved only to a certain extent; when they have the same electrophilic character, it goes to completion, with formation of a homopolar electrovalent bond.

Acceptance of the concept of the homopolar electrovalent bond is impeded by the fact that between equally electrophilic atoms a covalent link is energetically more advantageous. However, it is possible to imagine cases in which an electrovalent arrangement in the bond is bound to occur. The notion of an electrovalent structure in a bond between atoms (generally covalently linked) that differ little in electrophilic character, such as nitrogen and oxygen, sulfur and oxygen in "semipolar systems", where the covalent arrangement is in conflict with the octet rule:
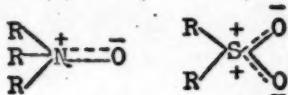
is generally accepted.

The octet rule and the fact that the lengths of the nitrogen-oxygen bonds in the nitro group are equal lead to the following formula:
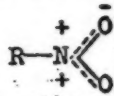
from which it follows that the electrovalent bond structure may turn out to be more advantageous even in cases where a covalent bond structure is not in conflict either with the condition that there should be sharp difference in the electrophilic natures of the atoms, or with the octet rule.

It is not difficult to show that in conjugated systems, e.g., in the benzene nucleus, electrovalent bonds are preferable to covalent bonds – even when the atoms have equal electrophilic character:
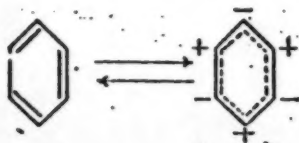
It is obvious that six electrovalent bonds are energetically more advantageous than three covalent links. Hence, cyclohexatriene is pseudomeric with benzene. However, in consequence of the equal electrophilic character of the carbon atoms (and as a result of the deformation of their electron clouds), the electrovalent bonds in the benzene nucleus are homopolar. Hence, the concept of a homopolar electrovalent bond within conjugated systems is far from being an absurdity – it has both an experimental and a theoretical basis.

The critics of the New Structural Theory assert also that the concept of hypermechanical, chemically-combining interactions in molecules is tantamount to a concept of mystical "life forces". Nesmeyanov writes [4]: "Chemical bonds have a combining function! What is this, a truism after the manner of Kozma Prutkov? Or is it an attempt to introduce into science some sort of special 'connective relationships' – some special chemical force that stands outside the ordinary, well-known attraction-repulsion interactions of electrons and nuclei and has the same right to a place in science as, in the last century, did the special life force that was to explain the specificity of biological phenomena .....It is this sort of pronouncement that Chelintsev considers to be an application of dialectical materialism in chemistry!"... "In his definition: 'reaction signifies discontinuous change in the chemical structure, preceded, accompanied, and succeeded by continuous changes in the distribution of atomic nuclei and electron density', Chelintsev again shows that he considers the quantitative changes in the distribution of nuclei and electrons only as an accompaniment, as it were, to the reaction and that he sees the causes of the appearance of a new qualitatively different state in something else – in that same mysterious chemical force that he calls a 'connective relationship'"....

Nesmeyanov continues: "It is obvious that a chemical reaction is above all the conversion of one or several discrete particles (molecules), which possess definite qualities, into one or several other discrete particles (molecules) that possess new, different qualities and that, at the same time, this qualitative jump is performed by means of continuous changes in the distribution of atomic nuclei and electron density .... From which, of course, it does not at all follow that chemical phenomena should be reduced to physical and electrical, not to say mechanical phenomena, in just the same way as biological phenomena are not reducible to chemical and physical phenomena, although they are dependent on them and although they do not contain any supplementary life force, but constitute a qualitatively different stratum of material movement".

From all this it is clear that Nesmeyanov does not admit the possibility of any other kinds of relationship between electrons and nuclei, apart from space-force relationships, or of any other kinds of change in chemical reactions, apart from continuous rearrangement of atomic nuclei and of electron density. The phenomenon of the discrete molecule, according to Nesmeyanov, is completely embraced within the concept of an electron-nucleus aggregate, and the phenomenon of discontinuous change in the qualitative nature of molecules during reactions – within the concept of the variation of the properties of molecules. Nesmeyanov admits the irreducibility of chemical phenomena to mechanical phenomena, but considers the regarding of a chemical bond not only as "attraction-repulsion interactions of electrons and nuclei", but also as a relationship of chemical combination to be tantamount to the admission of the existence of a "mysterious" "life force".

None of this is in accord with the philosophical meanings of the concepts of discreteness, discontinuity, quality, quantity, and property. Nesmeyanov's arguments do not differ in any way from the usual arguments of mechanists who reduce the concept of quality to that of quantity, the concept of continuity to the concept of discontinuity, and the concept of the discontinuous, step-wise, qualitative change in the structure of a thing to that of a change in its properties.

The Butlerov concept of hypermechanical chemical structure is a concretization of the Engels concept of hypermechanical chemical movement. Chemical movement differs from mechanical movement in the respect that it does not consist only in the redistribution of atomic nuclei and electron density, but is accompanied by step-wise changes in the chemical-combining relationships of the electrons and nuclei of the atoms, and of the atoms themselves – changes in chemical structure. Outside the concept of chemical structure (i.e., the integrated assembly of individual chemical-combining relationships of the atoms together with the atoms themselves, and electrons and nuclei forming the molecule, which is qualitatively distinct from the general space-force relations between atoms etc., within the molecule and between molecules) the concept of hypermechanical chemical movement has no meaning. In the Butlerov concept of chemical structure we are given an attempt at learning the hypermechanical laws that apply to chemical phenomena. It is not attempts at understanding hypermechanical phenomena that lead to agnosticism and idealism, but mechanism.

Apart from the allegations considered above, the criticism of the New Structural Theory contains a number of particular remarks, which are brought together in Nesmeyanov's article "Reply to G. V. Chelintsev" [5]. Nesmeyanov considers that the occurrence of the leveling-out of bonds in the carbonate ion directly proves the truth of the concept of the delocalization of electron orbitals and that this phenomenon cannot be expressed in the formulas of the New Structural Theory. However, the New Structural Theory gives the formula of the carbonate ion as [6]:

thus showing the invalidity of Nesmeyanov's allegation in both of its parts.

Also, Nesmeyanov points out that the orbit-contact formula for benzene is not in accord with the evening-out that occurs among the carbon–carbon bonds in the molecule. However, even if one ignores the concept of the homopolar electrovalent bond and erroneously interprets, as Nesmeyanov does, the pluses and minuses of the orbit-contact benzene formula (see above) not as indicating the charges on the atoms, but in the sense of bond polarity, then even in this case the intercarbon links in the formula become evened out with respect to length. In as much as Nesmeyanov gives as examples of the non-accord of the New Structural Theory with the phenomenon of the leveling-out of bonds the formulas of the carbonate ion and benzene, it is evident that the question in dispute is the leveling-out of bonds with respect to length and not with respect to the distribution of electron density between the carbons (in the carbonate ion all the bonds are polar). Nesmeyanov's assertion about the

non-accord of the orbit-contact formula of benzene with the phenomenon of the leveling-out of bonds is therefore erroneous not only in essence, but also logically.

Nesmeyanov further asserts that since the New Structural Theory makes use of the octet and tetrahedral rules it rejects the possibility of the existence of the molecules of phosphorus pentachloride, molybdenum octafluoride, etc. However, the rules of the octet and tetrahedron exist independently of the New Structural Theory, and no one has attributed to them the significance of general laws.

Nesmeyanov then rejects the New Structural Theory on the grounds that according to the theory stable aromatic molecules of cyclobutadiene and cyclo-octatetraene should be possible. However, in the New Structural Theory it was shown that [7] "aromatic rings have either five or six members because the energy required to change the valency angles in the formation of larger or smaller flat rings exceeds the gain in energy due to aromatic bond formation". Indeed, the examples of benzene, the carbonate ion, the guanidine ion, the carboxyl ion, and the nitro group show that double electrovalent-covalent (semipolar) bonds are arranged in one plane and form valency angles (for carbon or nitrogen) approximating to 120°. Thus the cited allegation of Nesmeyanov is simply a misunderstanding.

Nesmeyanov asserts also that in the New Structural Theory oscillation concepts are employed. Without these concepts it would be impossible, it is alleged, to understand how the orbit-contact formula of anthracene could be made to accord with the absence of a dipole moment in its molecule. These concepts are used directly, it is alleged, in my treatment of the absence of isomers in monosubstituted benzene:
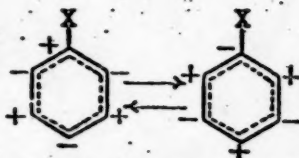
In as much as the concept concerning oscillation is a primitive representation of the delocalization of orbitals, the New Structural Theory, being based on the law of localization of orbitals, must be regarded, according to Nesmeyanov, as inconsistent. However, the New Structural Theory has no need for oscillation concepts. The absence of a dipole moment in anthracene is to be explained by the homopolarity of its bonds, and the absence of isomeric monosubstituted benzenes — by its pseudomeric relationships [8] (in consequence of their ready interconversion, only the more stable structure exists).

Nesmeyanov points out, finally, that the orbit-contact formula of benzene is equivalent to the formulas of Vorländer and Berkenheim, which have long been rejected. It is generally known that Vorländer and Berkenheim placed pluses and minuses on the carbons of the benzene nucleus and that the phenomenon of "alternating polarity" was discovered long before the coming of the New Structural Theory. However, these formulas were rejected because they could not be defended outside the concepts of orbit and contact bonds that are given in the New Structural Theory. The criticism by Nesmeyanov of the orbit-contact formula of benzene is a proof of this — it is quite justified when applied to the formulas of Vorländer and Berkenheim, but invalid in this case. As he does not discern the difference between these formulas and does not take

account of the content of the New Structural Theory, Nesmeyanov is, in fact, criticizing not this theory, but Vorländer and Berkenheim's theory. Such criticism is easy, but it misses the mark.

I must thank Nesmeyanov [9] for only two justifiable critical remarks. In the first place, I acknowledge that my application of the unverified assertion by Goldschmidt [10] concerning the presence of an axis of third-order symmetry in crystalline benzene was erroneous. In the second place, I acknowledge that my statements concerning the causes of coplanarity in conjugated and aromatic systems were erroneous also. Nevertheless, these errors, like many others which may be found, in no way affect the basic principles of the New Structural Theory.

In the same article "Reply to G. V. Chelintsev" Nesmeyanov writes: "Why does Chelintsev never make use of this 'New Structural Theory' for scientific purposes (and only for the purpose of unrestrained self-praise)........ Why on the basis of the 'New Structural Theory' has its author not made an attempt to make even a very limited prediction of new facts, not to speak of the verification of such predictions by experiment? It seems to me that there is only one answer. The author of the theory is convinced of its worthlessness — and so am I".

The question of why I do not use the New Structural Theory for scientific purposes is an obscure one. Is not my use of this theory for solving the question of the structures of hundreds of thousands of conjugated compounds, for confirming the truth of Butlerov's dialectical-materialistic teaching concerning chemical structure, for refuting the sterile Machist mesomerism-resonance theory, and for the elimination of servility and Machism from Soviet chemical science — is not my use of this theory for these purposes indeed an application of the theory for scientific purposes? As far as my conviction of the worthlessness of the New Structural Theory is concerned, is it really possible to suppose that for a number of years I could bear the whole weight of the struggle with the Ingold-Paulingites that were monopolizing Soviet chemical science, if I were not deeply convinced of the correctness and usefulness of my ideas?

There remains the question of the possibilities of prediction in the New Structural Theory. It is a great pity that this question was not put at the correct time with respect to the theory of resonance. It was several years before Nesmeyanov admitted that "The explanations given by resonance theory are illusory and, at the best, consist only of descriptions by means of an assembly of formulas" [11]. Evidently, for the determination of the possibilities of prediction in a theory, time and practice are required.

Nevertheless, let us examine what claims may be made from the New Structural Theory. It is here necessary to take into account that the New Structural Theory and mesomerism-resonance theory cannot be placed in the same category as the structure, stereochemical, co-ordination, and electron theories, with respect to their role in chemistry. Each of the latter theories reveals the laws of one or another separate variety of chemical particle (structural isomers, stereoisomers, complex compounds, radicals, and ions), and hence its formulas are suitable for the prediction of hitherto unknown particles.

The New Structural Theory and mesomerism-resonance theory did not come into being by virtue of their application to some newly discovered separate

variety of particle that did not come within the scope of previous theories. In this sense, they cannot predict anything new. However, it does not follow from this that they cannot be suitable for the prediction of a separate variety of particles. In as much as each of them is an attempt at uniting together all the theories enumerated above, it is bound to preserve all their possibilities of prediction. Consequently, the evaluation of the possibilities of prediction for the New Structural Theory and mesomerism-resonance theory with regard to a separate variety of particles can be done by suitable comparison of one theory with the other.

The superiority of the New Structural Theory is here obvious. There are preserved in it the laws and rules of the chemical combination of atoms and of atoms, electrons, and nuclei in particles which are revealed in the above-enumerated theories and embodied in their formulas — laws of the localization of orbitals and bonds, rules of valency numbers, octets, and tetrahedra, of coordination numbers, co-ordination, and octahedra. There are preserved in it the affirmation of the truth of these formulas and of the correspondence of each formula to one real particle, and therefore of the possibility of predicting hitherto unknown particles corresponding to formulas that have not been assigned to known particles. On the contrary, the concept of the delocalization of orbitals that lies at the basis of mesomerism-resonance theory logically leads to a rejection of the laws and rules mentioned, to affirmation of the ficticiousness of the formulas referred to, and to prediction of an unlimited number, by comparison with the number of real particles, of distributions of atomic nuclei and electron density, i.e., to complete loss of the prediction possibilities of the above-enumerated theories.

If with respect to the prediction of separate varieties of molecules the New Structural Theory preserves only the possibilities of classical theory, then with respect to the prediction of new facts in general, it will be fruitful in the highest degree. The replacement of the erroneous formulas of hundreds of thousands of conjugated compounds by correct formulas is bound to lead to the enrichment of the predicting possibilities of the theory of chemical structure. Time and practice will lead not only to confirmation of the truth of the New Structural Theory, but also to the revelation of its practical fruitfulness.

In spite of its imperfections, the New Structural Theory, even in its present form, is incomparably more practical than mesomerism-resonance theory. It will serve as a reliable basis for chemical theory at the present stage of the development of structure problem.

It is necessary to realize clearly that the possibility of avoiding the usual erroneous formulas for conjugated compounds provided in the formulas of Ingold and Pauling does not help, but hinders the development of chemical theory. It should be understood that no other formulas for the chemical structure of conjugated compounds apart from those of the New Structural Theory can exist on the plane of modern electron-nucleus concepts. When the significance of these formulas has been assimilated, then it will be possible to simplify them, for example:

benzene   butadiene   vinyl chloride

and they will then not only be true representations of conjugated compounds, but also practically convenient methods of representation.

Soviet chemical theory must be freed from the influences of bourgeois theory and must develop within the plane of Butlerov's dialectical-materialistic teaching concerning chemical structure.

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"CONTACT BONDS" AND THE "NEW STRUCTURAL THEORY"

A. N. Nesmeyanov

In his reply to critics of the New Structural Theory [1], Chelintsev is concerned with certain of my critical pronouncements [2]. He admitted only two of the concrete critical inferences that I made, and these directly concerned the nature and formation of "contact bonds". These were: the error made by Chelintsev in attributing an incorrect axis or third-order symmetry to crystals of benzene in his considerations concerning the structure of the benzene molecule, and his error in making the assertion that the coplanarity of olefin, aromatic, and similar molecules can be derived from the properties of the contact bond, as being a bond of octahedral origin. However, he considers that these mistakes are special cases, admits that his New Structural Theory still contains many similar mistakes, and is convinced that these errors do not affect the basic principles of his theory. Certain other of my concrete criticisms, all concerning the same contact bond, he passes over in silence (e.g., the tetrahedral character of HgI_2, which corresponds, according to Chelintsev's theory, to an orbit structure like that of CH_4 and therefore dissociates tetrahedrally built complex compounds from a group of compounds that are obviously closely related — the octahedrally built complexes; the phenomena of substitution orientation in aromatic compounds as a whole, and in five-membered heterocyclic compounds in particular; and so on).

He gives answers to a number of concrete critical remarks, and as I cannot agree that these answers are satisfactory and as I cannot regard the errors pointed out by me and admitted by Chelintsev as special cases, I am forced to continue my discussion of the "New Structural Theory".

The New Structural Theory is based on the recognition of two types of bond — "orbit" bonds and "contact" bonds. Orbit bonds, as described by Chelintsev, have not a single characteristic that distinguishes them from ordinary covalent bonds. Thus, orbit bonds differ from covalent bonds only in name. Hence, it is not these that lie at the basis of Chelintsev's theory. This is the part played by contact bonds. The latter "are subject to the rules of coordination numbers, of coordination, and of the octahedron". [1] "They are possible between coordinately unsaturated oppositely charged atoms, between coordinately unsaturated neutral atom-dipoles, and between the ones and the others, and here in the character of atom-dipoles we meet atoms with incomplete octets of valency electrons and atoms with unshared electrons in their valency shells. The main difference between charged atoms and atom-dipoles is that the former can form contact bonds directed towards all the corners of an octahedron (within the limits of their coordination numbers), while the latter form contact bonds only in directions corresponding to maximum and minimum electron density in their volumes. The coordination rule is the rule of opposite polarity of atoms in the direction of the contact bond".

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[1] Here and later, the quotations are from Chelintsev's book [3].

Contact bonds "are built by the deformative sharing by two atoms of electrons that are not orbitally shared". "The concept of the contact bond corresponds to the concepts of 'physical', 'ionic', 'electrovalent', 'ion-dipole', 'complex', 'molecular', and 'hydrogen' bonds."

"The concepts of orbit and contact bonds differ from the above-mentioned corresponding concepts in that the qualitative distinction between them and between either of them and Coulomb attractive forces (e.g., 'indirect' bonds with atoms in the second co-ordination zone) is expressed in their structures. Both orbit and contact bonds have not only attractive, but also combinational (deeper in the first case) significance and determine in a fundamental way the peculiar properties of the orbit- or contact-bond particles. Both orbit and contact bonds possess not only Coulomb (when they are polar), but also 'intrinsic' energies (more significant in the first case), being respectively — the energy of electron-orbit sharing ('exchange', 'resonance') and the energy of the deformative sharing of electrons; these determine the discreteness of the orbit- or contact-bond particles. Attractive forces act both between combined, and also between uncombined electrons, nuclei, and atoms, and these forces determine the properties of the particles to a considerable extent, but, in distinction to the bonds, they do not in any way determine the qualitative peculiarities of the molecules."

The central points of Chelintsev's theory are the postulation of homopolar contact bonds and the application of orbit-contact bonds to explain the properties of organic unsaturated, aromatic, and other compounds, in which the Butlerov theory of structure assumes a double bond. This ascribing to a contact bond of possible homopolarity is extremely important, as will be seen already from Chelintsev's "reply", since without this assumption the applicability of the New Structural Theory to the chemistry of unsaturated and aromatic compounds, i.e., to the greater part of organic chemistry, immediately disappears. With regard to the chemistry of saturated compounds — this is the field of orbit, i.e., covalent bonds, to which the New Structural Theory brings nothing new. Thus, without homopolar contact bonds Chelintsev's theory cannot exist.

Also, according to Chelintsev, the treatment of double bonds in aromatic and unsaturated compounds as containing the same sort of contact bonds that are characteristic for inorganic structures, which "are subject to the rules of co-ordination numbers, of co-ordination, and of the octahedron", leads to a unification from one single point of view of organic and inorganic chemistry. However, the only actual manifestation of the nature of the contact bond pointed out by Chelintsev in aromatic, unsaturated, or similar compounds (if we do not count homopolarity — for indeed it is not, according to Chelintsev, specific for the contact bonds, being, in fact, more characteristic for the orbit bond) was, before my critical review, the coplanarity assumed by Chelintsev for these structures, which was alleged to follow from the octahedral nature of the contact bond. That is why a withdrawal from this position, which undermines the unification of organic and inorganic chemistry on the basis of contact bonds with their identical properties for both fields, is not an exceptional, particular case for the New Structural Theory. What, after this withdrawal, has the "contact" bond in ethylene in common with the "contact" bond in common salt, the ion Hg_4^{--}, or octahedral complexes? What we are talking about, of course, is something in common that stands in contrast to an orbit bond.

Neither is Chelintsev's error concerning an axis of symmetry of alleged third order in benzene to be considered as an exceptional case for his theory. The essential point about this mistake for the theory is not that the axis of symmetry of the crystal (which, at the same time, is given wrongly as an axis of third order) is used as an argument for the symmetry of the molecule of ben-

zene. The essential point is that Chelintsev cited an axis of <u>third-order</u>
symmetry for confirmation of his structural formula for benzene.
From this it is clear what sense he attributed (at least, at the
time when he wrote the book that I criticized) to the signs +
and − that distinguish the adjacent carbon atoms of benzene in
Chelintsev's formula. He now says that there is no distinction
between the carbons, that his formula, as also the actual mole-
cule, has sixth- and not third-order symmetry, that the contact
bonds of benzene are homopolar, and that + and − denote not polarity, but the
fact of the excess or deficit of an electron, as compared with the nuclear
charge. But argumentation on the basis of an axis of third-order symmetry is a
definite and convincing thing! It contradicts these assertions. Hence my crit-
icism of Chelintsev's formula bracketed with the formulas of Vorländer and Berk-
enheim does not "miss the mark", but is right on the bull's eye. The withdrawal
from the assumption of an axis of third-order symmetry in benzene which resulted
from this hit is already a new point of view. Within the bounds of Chelintsev's
theory it is inseparable from the postulate of the homopolarity of the contact
bond. In his objections, Chelintsev attempts to give arguments in favor of
what he himself calls the absurd concept of a homopolar electrovalent bond, as
it would appear at a first glance [1]. The matter remains the same however, not
only just at the first glance. So long as a contact bond is understood as an
ionic bond, just as a covalent bond is equivalent to an orbit bond − all is in
order. When in a molecule of ionic structure $A^+ B'$ we assume the polarization
of the electron cloud of the anion by the cation, we again are concerned with
methods of looking on these matters that are understood and have been applied
for a long time in science.

If the atoms A and B are identical, then we may assume an unstable state
$A^+ A'$. However, if we imagine polarization of the anion A' by the cation A^+
in such a way that the electron density will be distributed symmetrically about
both A atoms (with a plane of symmetry perpendicular to the line A − A in its
center), then the molecule would be homopolar, non-dipolar, but at the same time
the electrons of the shell of the former anion A' would continue to belong to it
and only to it, which means abandoning science and assuming purely juridical
relations between the two A atoms. This is what is meant by a homopolar contact
bond. Withdrawal from the axis of third-order symmetry and acknowledgement of an
axis of sixth-order symmetry in benzene is significant in that it is an acknow-
ledgement that these juridical relations leave no material trace in the molecule.

Is this really materialism? Is this not a manifestation of free will, if
not of the electron, then of the nucleus? Have these "connective relationships"
of electron and nucleus really got very far away from the life force? If it were
not for these juridical relations, then with such a complete leveling-out of
electron density, $A^+ A'$ would change into A − A with a covalent, or as Chelintsev
wants to call it, orbit bond. Thus, the ability of a contact (i.e. electrovalent)
bond to be homopolar, which is essential for Chelintsev's theory, is illusory and
can in no way be justified by means of the examples cited by Chelintsev, such as
nitrobenzene, with leveled-out electron densities around the two oxygen atoms,etc.

The above-mentioned juridical relations comprise, in fact, in this special
case of electron and nucleus, the "connective relationships" that, according to
Chelintsev, exist in the molecule in addition to the force relationships and, as
far as one can understand his ideas, condition the specificity of chemical phe-
nomena! Such a point of view, in my opinion, is indeed extremely similar to a
recognition of a special life force, which is supposed to condition the specific-
ity of biological phenomena. I do not doubt that Chelintsev ought to turn away

from this point of view and so from the homopolarity of the contact bond (in other words, the non-polarity of the polar bond) together with all the consequences of this that arise in his theory.

As regards the point of view that I have expressed: although Chelintsev quotes my text correctly, he gives it a warped commentary. "The phenomenon of the discrete molecule, according to Nesmeyanov," he writes, "is completely embraced within the concept of an electron-nucleus aggregate, and the phenomenon of discontinuous change in the qualitative nature of molecules during reactions - within the concept of the variation of the properties of molecules" [1]. I have said nothing from which such an inference could be made; it contradicts my assertion, cited by Chelintsev, that "... it does not follow at all that chemical phenomena should be reduced to physical and electrical, not to say mechanical phenomena..." [2]. I spoke of chemical reactions as "the conversion of one or several discrete particles (molecules), which possess definite qualities, into one or several other discrete particles (molecules) that possess new, different qualities...." [2], but Chelintsev in his commentaries tries to allege that I am of the opinion that the concept of chemical reaction is to be reduced to the concept of the changes in the properties of a molecule. What is this — lack of understanding by Chelintsev of the difference between the concepts of quality and of property, or a special method of discussion? How it is to be called I leave the reader to judge. I consider that this method is in the same category as the declaration that all critics, present and future, of one's own theory are Ingold-Paulingites.

A molecule is, of course, a nucleus-electron formation[1], built up in a definite way[2], and no special forces, other than the electron-nucleus interactions known to physics, take part in its build-up; but from this, in no sense should the inference be made, which Chelintsev wishes so much to ascribe to me, that the essence of a molecule is limited to this and that the essence of chemical change amounts to the redistribution of the nuclei and electrons of the reacting molecules. The essence of reaction, the essence of chemical movement, lies in the fact that from certain chemical substances as a result of reaction other chemical substances are formed, and this essence cannot be reduced to anything else, but constitutes the specific object of study of chemical science. Nevertheless, this essence of a higher (compared to physical and mechanical) form of movement has no need of any special mechanism, maintaining it and conditioning it, other than the known interactions of nuclei and electrons.

Indeed, for example, in this dispute between Chelintsev and myself, the essence is not in the mechanical movement of the pen over the paper, not in the muscular contractions that conditioned it, not in the biochemical and electrophysiological processes in the brain and nerves that preceded and accompanied these acts, and so on, but the thoughts that are expressed as a result of and through the means of these processes by each of us, thoughts that with respect to both their course and their mutual relations are subject to special laws. Our dispute, therefore, is in no way to be reduced to all the enumerated biophysical and biochemical acts, and others like them. But it would be an obvious idealistic fallacy to seek as a result some special discussion force or special discussion relationships between cells of the brain with which Chelintsev must

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[1] But not an aggregate, for an aggregate is a chance conglomeration, and a molecule is a strictly organized formation — a structure. Although Chelintsev saddles me with the word "aggregate", I have never used it.

[2] E.g. in the sense of interatomic distances, energy levels, etc., but not in the sense of the presence of special mysterious properties in the nucleus and

be endowed in such great measure. In just the same way the essence of thermal movement cannot be reduced to mechanical movement, in spite of the fact that the latter must be placed at the basis of thermal movement. Thermal movement has its own peculiar laws, which are studied by thermodynamics. The concept of temperature cannot be applied to a single molecule and its movement. The second law of thermodynamics has no meaning for two or three molecules. Nevertheless, it would be absurd to seek some sort of special "thermal relationships" between these two or three molecules and to try to explain the laws of thermodynamics from these relationships. Similar considerations apply also to chemical change and its carrier — the molecule.

After all that I have said I may repeat that, if by "connective relationships" Chelintsev understands that specificity of a higher (than mechanical and physical) form of movement, which, indeed, forms the subject of the study of chemistry and is manifested, above all, in chemical reaction, then we have an obvious self-evident thing — a truism. If, however, by connective relationships is meant some specific force that stands outside the known physical interactions in the molecule or in the combination of nucleus and electron, then this, of course, means that we are on our way to the introduction into chemistry of the analog of life force. Unfortunately, Chelintsev's "reply" leads one to believe that he holds this second view. If this were not so, there would be no purpose in seeking "connective relationships" acting in the opposite sense to force relationships in the interaction of nucleus and electron, and those relationships of nucleus and electron (in a contact bond) that we have called juridical would not have been postulated. We will refer here to the quotation from Chelintsev's book that we made on p. 215; it gives a very clear illustration of what we have said (I will not go into Chelintsev's allegation that bonds have not only Coulomb energy, but also intrinsic energies ["exchange", "resonance"]). Thus, Chelintsev's whole conception is not "in accord with the philosophical meanings of the concepts of discreteness, discontinuity, quality, quantity, and property".

I will pass now to the remainder of my "particular" remarks that have been the subject of counter-objections on the part of Chelintsev. Chelintsev, in bringing forward his leveled-out formula for the CO_3 ion, has in no sense disproved my arithmetic; his formula, like any other that takes into account the actual symmetry of the CO_3 ion, expresses the fact that on each oxygen atom there is 1/3 of the charge of each of the two electrons of the anion and that an electron, therefore, is shared between more than two atoms. Only in this, indeed, consists the "delocalization" of which we are talking.

In his objections concerning the leveling-out of bonds in benzene, Chelintsev holds entirely to the idea of the homopolarity of contact bonds and to the ideas of the juridical appurtenance relationships of electron to nucleus, which leave no material trace. As regards this question, I refer the reader to p. 216.

Chelintsev writes further that the octet and tetrahedron rules exist independently of the New Structural Theory (this cannot be disputed — A.N.) and that no one has attributed to them the significance of general laws. This is not true. Such significance was attributed to them by none other than Chelintsev (see quotation on p. 215.) In fact, if Chelintsev had deduced the geometry of the contact bond not from octahedral complexes, but, for example, from the tetrahedral $HgI_4^{"}$, then the result would be that (owing to the coincidence of the tetrahedral geometry of orbit and contact bonds) a tetrahedral configuration would have

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electron, which compel the latter to remember that even when it is far removed from its master-nucleus and has come into the sphere of action of another nucleus, it still belongs to its master.

particular stability in olefins and aromatic compounds, which is an absurdity.

y criticism of Chelintsev relating to the prediction by his theory of the in .bility of benzene and the stability of the non-existent cyclobutadiene is not at all a misunderstanding, as Chelintsev supposes. In fact, Chelintsev brings forward arguments (as he now agrees – erroneous ones) to prove the planarity of aromatic structures from the postulate that the contact bond is built according to the octahedral principle, i.e. that the angle of four contact valencies is 90° (the same also for two) and that they lie in one plane. This means that, in his opinion, the geometry of the contact bond must actually determine the configuration of an aromatic system, and not the geometry of the orbit bond. From this it will be seen that my inference about the "prediction" and my criticism were altogether valid and logical.

If at that time Chelintsev had held the view expressed by him in his "reply" on p.210 to the effect that the valency angles of covalent bonds are more stable than the valency angles of electrovalent bonds, then he would not have made the inference of the planarity of benzene, due to contact bonds. Benzene would then have been like cyclohexane. The assertion that "the examples of the carbonate ion, the guanidine ion, the carboxyl ion, and the nitro group show that double orbit-contact (semipolar) bonds are arranged in one plane and form valency angles approximating to 120°" is nothing more than a statement of experimental fact, in no way derived from the "New Structural Theory", or from the geometry of orbit or contact bonds. This assertion can have only one relation with the New Structural Theory, that of an additional independent postulate. The necessity for the acceptance of this postulate by Chelintsev owing to the collapse of his explanation of the planarity of aromatic structures and of olefins has been pointed out by me in my "Reply to G.V.Chelintsev.' [2].

Actually, the geometry of the contact bond – its construction according to the octahedron principle – has remained in force for Chelintsev, even after he has acknowledged his error in the explanation of the planarity of aromatic structures (this error has its basis only in the forgetting of the fact that two straight lines that intersect a third are not bound to lie in one plane). At least, he does not say anything about withdrawing this property of the contact bond.

It is doubtful whether there is any need to go into the remaining statements by Chelintsev in support of the New Structural Theory; they are equally unconvincing.

Objections to the postulates of the New Structural Theory will be removed only by the withdrawal of these postulates by their author. When Chelintsev renounces the unusual and unnatural properties of the contact bond, converts it into an electrovalent bond, expels it from unsaturated and aromatic structures, and replaces it in these structures by a double bond, with its propensity for being leveled out in conjugated systems, everything will be in its place. While this remains undone and the New Structural Theory differs (in the properties of the contact bond) from the old, this theory is bound to lead, at least in some respects, to conclusions that differ from those of the old theory, and they must be verified by experiment. I have pointed out some such conclusions that are in direct conflict with experiment. Chelintsev has withdrawn these conclusions together with certain properties of the contact bond, but it is essentially from these properties, taken as an associated whole, that the "New Structural Theory" is made up.

Our reproach to Chelintsev, that he himself refuses to make any inferences from his theory for verification by experiment, remains in full force. He is

convinced, however, so he writes, that "the New Structural Theory and mesomerism-resonance theory did not come into being by virtue of their application to some newly discovered separate variety of particle that did not come within the scope of previous theories. In this sense, they cannot predict anything new" [1][1]. Comment, as they say, would be superfluous!

Under such conditions, our demand of G. V. Chelintsev that he should not only verify inferences made from the New Structural Theory by experiment, but should also attempt to predict some new facts on its basis is clearly excessive.

Our chemistry must be thoroughly cleared of all the unhealthy influences of corrupt bourgeois philosophy and science. It must be cleared also of vulgarization of home origin.

I do not doubt that by the joint harmonious efforts of Soviet chemists this will be done and that Soviet chemistry will develop still more widely and more brilliantly, utilizing in full our precious classical inheritance of Russian chemical science, the most recent results of chemistry and physics, and the great philosophy of Marxism-Leninism.

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[1]The emphasis is mine — A.N.

CHRONICLE

At the Academy of Sciences of the Armenian S.S.R. in Erevan on October 24-31, a conference was held on the problem of the relation between chemical structure and pharmacological activity as a basis for the search for new medicinals.

This conference, the first in our Union, was organized excellently by the pharmaceutical laboratory of the Academy of Science of the Armenian S.S.R., under the directorship of Corr.Mem. Prof. A.L. Mndzhoyan.

Scientific workers from Moscow, Leningrad, Sverdlovsk, Baku, and other parts of the Union attended the conference.

The large number of papers (more than 20) drew a big audience and called forth lively discussion, which considerably helped in the elucidation of very important questions that are exercising the minds equally of chemists, pharmacologists, physiologists, and clinical physicians. The absence of biochemists was noted with regret, and the conference resolved to take measures in future to bring clinicists and biochemists together in this work. The importance of the latter is very great for the solution of questions closely related to the properties of medicinals and to the role of the substrate of the organism, which directly reacts with the chemical compound.

The responsible role of clinicists in the characterization of medicinal preparations is beyond doubt, and their participation in the solution of the problem of the relation between chemical structure and biological action is quite essential in order to settle quickly the important question of the depositing of the chemical preparation in the treasure house of the pharmacopeia.

Of the large number of papers it is possible to note only a few that are of leading importance. As an introduction, a short historical sketch was given of the development of the pharmaceutical chemicals industry in our country.

Honored Scientist Dr. N.V.Lazarev gave the introductory paper on certain general questions in the study of the relation between structure and activity. Reg.Mem. Acad.Sci.USSR Kh.S.Koshtoyants gave an interesting and circumstantial account of his experimental physiological work concerning the significance of the sulfhydryl groups in the substrate of the living organism, and he emphasized particuarly the importance of I.P.Pavlov's teaching for the rational conduct of pharmacological investigations. Kh.S. returned to this theme on several occasions in his many speeches. "The Chemistry and Pharmacology of Choline-negative Agents" was treated in an illuminating paper by Prof. M.Ya.Mikhelson (Leningrad). Corr.Mem of the Academy of Medical Sciences Prof. V.M.Karasik (Leningrad) analyzed in detail the fundamental variants of the competitive interrelations between substances of similar chemical structure and behavior.

An interesting pharmacological paper was given by Prof. M.D.Mashkovsky (Moscow) on chemical structure and antihistamine activity; he considered that the utmost attention must be given to the importance and necessity of studying the pharmacological behavior of medicinals under test from every side.

The director of the pharmaceutical laboratory of the Acad. Sci. U.S.S.R., Corr. Mem. Prof. O. L. Mndzhoyan gave a circumstantial paper on the relation between chemical structure and anesthetic activity in organic compounds. In this paper, the review of original work in the Erevan laboratory is particularly valuable. This communication, and also interesting reports by the laboratory workers themselves, revealed the caliber of the young laboratory staff and gave every reason to believe that chemical work was being carried on at a high level in close contact both with local pharmacologists, and with many Leningrad workers.

A very important communication was made by Dr. (med. sci.) O. G. Birger (Moscow) on combined chemotherapy. As is well known, in the treatment of many diseases due to micro-organisms, sulfamide, antitubercular, and other preparations give rise to resistant strains of organisms, which are not susceptible to these drugs. Dr. Birger, giving many examples, showed that a good method of dealing with this troublesome phenomenon could be found in combined chemotherapy.

In a brilliant paper, Prof. Shamyakin (Moscow) examined in detail the question of the structure and biological activity of antibiotics. These compounds, which in a very short time have come to form a new important section of organic chemistry, were treated with exceptional lucidity and fulness.

Of the other chemical papers we may mention that of Prof. O. Yu. Magidson (Moscow) concerning the structure and chemotherapeutic activity of sulfamide preparations. Prof. Magidson is one of our greatest experts on this question and has done much valuable and original work in this important field, in which he has established the principal chemical regularities.

Other interesting papers were that of E. S. Golovchiskaya (Moscow) on derivatives of caffeine with various substituents in the 8-position and that of M. N. Shchukina (Moscow) on her very original investigations on the synthesis of antitubercular chemotherapeutical substances.

In connection with M. N. Shchukina's paper, we may mention also the interesting communication of V. G. Afrikyan (Erevan) on the chemical structure and antitubercular activity of certain amides.

It is not possible to enumerate all the interesting questions dealt with at the conference; they provide rich material on the fundamental question of the relation between chemical structure and biological activity in organic compounds. The conference noted also many short-comings in chemical work and pharmaceutical investigation and made valuable proposals for the elimination of great and small defects both in the scientific research institutes and also in other scientific and industrial organizations. Resolutions were carried unanimously relating to the necessity for carrying on scientific work on the basis of the teaching of Butlerov and Markovnikov, for paying greater attention to the study of the physical properties of organic compounds, and, in general, for carrying out the characterization of compounds more accurately and in greater detail in all respects. The pharmacological study of medicinal preparations must be carried on in the spirit of the fundamental theories of I. P. Pavlov, who laid down all the prerequisites for the creation of rational pharmacology and experimental medicine. A very important proposal was made by the conference concerning the setting-up of a general center for the co-ordination of all the organizations working on the problem of "chemical structure and activity", and it was decided to make a request to the Presidium of the Acad. Sci. U.S.S.R. concerning the organization of such a center.

The conference provided a large amount of material on the problem of "structure and activity", resolved to print the "Transactions of the Conference" as soon as possible, and proposed that a second such conference should be called in the near future to consider the question of structure and the biological activity of natural compounds.

CONFERENCE ON THE BASIC PROBLEMS OF PHOTOGRAPHIC SCIENCE

During the period June 29 – July 4, 1951 at Odessa, there was held an all-union conference on the basic problems of photographic science, organized by the Committee on Photographic and Cinematographic Science of the Div. Chem. Sci. of Acad. Sci. U.S.S.R. and by the I.I. Mechnikov State University of Odessa.

Participants in the conference included many representatives of our scientific institutes and of industry. Delegates and speakers came from several institutes of the Acad. Sci. U.S.S.R., from the Institute of Organic Chemistry of the U.S.S.R., from the Moscow State University, from the Odessa State University, from the All-union Research Institute for Cinematography and Photography, from the State Optical Institute, from the Leningrad Institute of Cine-engineers, from the factories and studios of the Ministry of Cinematography of the U.S.S.R., and from many other such places.

Opening the conference, the president of the Committee on Photographic and Cinematographic Science, Prof. K. V. Chibisov, pointed out that this was the sixth all-union conference on photographic science. The first three conferences took place before the Patriotic War – in 1932, 1937, and 1941. At the end of the war, the work of convening all-union conferences fell on the newly created Committee on Photographic Science of the Acad. Sci. U.S.S.R. Since then, three further conferences have been arranged – the fourth, at Moscow in 1949, at which the scientific and technical applications of photography and cinematography were considered; the fifth in 1950, also at Moscow, which was devoted to questions of photography and cinematography in color; and, finally, the present, sixth conference on the basic problems of photographic science, called in Odessa. The choice of place for the sixth conference was not an arbitrary one – Odessa, as the seat of the Physics Research Institute attached to Odessa State University, is one of the scientific centers of the photographic field. This center was built up by the work of a senior Soviet physicist, Prof. E. A. Kirillov, who set up a school of scientific work and for 25 years has directed the research institute referred to. In calling the conference in Odessa, the Academy Committee on Photographic and Cinematographic Science has marked the twenty-fifth anniversary of the founding of the Odessa State University Institute of Physics and has called attention to the valuable work of Prof. E. A. Kirillov and his scientific school.

An extensive discussion was made at the conference of three basic problems in photographic science, which lie at the basis of all photographic technology, including also cinematography: 1) the nature of photosensitivity and of the latent photographic image, 2) optical sensitization, and 3) the process of photographic development.

In discussions on the nature of photosensitivity and of the latent photographic image (three sessions), an important place was occupied by the work of E. A. Kirillov and his students (S. I. Golub, A. S. Fomenko, Zh. L. Broun, M. E. Fonkich, T. Ya. Sere, A. B. Kotlyarovsky, and others; papers were read by E. A. Kirillov, Zh. L. Broun, and M. E. Fonkich). In this work, which is of

great interest for the theory of the latent image, it was shown that the absorption of photochemically and additively colored crystals of silver halide has a fine structure with a series of maxima over the whole region from 350 to 750 mµ. These maxima of light absorption closely correspond to the maxima of photoconductivity. It is interesting that the absorption maxima in the interval 450-540 mµ and at 600 mµ in the crystals of silver chloride, bromide, and iodide correspond satisfactorily, which points to the feeble influence of the crystal lattice of the basic material on the structure of the corresponding color centers. Analogous structures were found not only for free crystals but also for exposed silver bromide photographic emulsions. On the basis of these investigations it was concluded that, as well as colloidal particles, atomic centers and complexes of two, three, or more atomic centers exist in colored silver halide. The atomic centers, on increasing the exposure or the degree of dispersion of the silver, grow into colloidal centers. The centers that give rise to the fine structure are preserved even with exposures that produce intensive coloring. The spectrum of centers that are distributed within the crystal has an analogous structure, but with a different distribution of intensities. The absorption of a photographic emulsion that has not yet been exposed to light also has a fine structure. Thus, centers with which a fine structure is associated arise not only at all stages of the photochemical process, but also during the ripening of the photographic emulsion. Investigations were made also of the intensification of the latent photographic image under the action of light (Zh. L. Broun). It was found that a weak second exposure converts sub-latent centers into developable centers, while having little influence on the remaining particles of the latent image.

K. V. Shalimova discussed the nature of the centers of luminescence in silver halides. In this work an investigation was made of the luminescence of the chloride, bromide, and iodide of silver at the temperature of liquid air. The phosphors were obtained by sublimation of the respective silver salts. It was found that silver could be used as an activator of the luminescence. On the basis of the results obtained it was concluded that silver atoms are the source of the luminescence of silver halide phosphors containing both small and large amounts of activator. Further increase in the content of silver atoms in the lattice of the phosphor under the action of light leads to a state of the activator characterized by an absorption spectrum and absence of luminescence. This activator, which is in an unstable degenerate state, may be compared with the silver atoms that are feebly attached to the lattice of the crystal, the absorption of which was studied by E. A. Kirillov. The further formation of silver atoms under the action of light leads to the formation of colloidal silver particles, which give the absorption of color centers and do not show luminescence.

F. F. Volkenshtein reported on color centers in silver halide crystals and developed new ideas concerning the mechanism of the photochemical development of color in crystals and the physical nature of color centers. Attention was drawn to the fact that at the present time there is not sufficient evidence to enable a final choice of a model of an F-center to be made. The concept of Ya. I. Frenkel and Pohl, according to which an F-center is a silver atom (an electron near to an interstitial silver ion), and the concept of de Boer, according to which an F-center is an electron situated in a vacant anion space, have equal right to existence.

P. V. Meiklyar read a paper on the nature of the photochemical and photoelectric sensitivity of silver halide crystals and of the photographic layer. Comparison of the photoelectric sensitivity curves of silver halide with the spectral sensitivity curves of photographic layers of the same composition

leads to the conclusion that the maximum of the spectral sensitivity curves in the blue-violet and near ultraviolet regions of the spectrum is determined by light absorption by F-centers (which in silver halide crystals are analogous in nature to the F-centers of alkali halide crystals). In silver halide crystals, F-centers may be formed not only by the action of light or heat, but also during the preparation of the emulsion and as a result of interaction of labile sulfur present in the gelatin with silver halide. The F-centers formed partially combine together to form centers of metallic silver. When the crystals in the emulsion absorb light, electrons are liberated both from F-centers and from halide ions. However, the F-center photo-effect plays a predominant part, since it occurs with a greater quantum yield.

An interesting paper on the relation between the systems of optical levels in ionic crystals and their X-ray absorption spectra was read by A. I. Kostarev. K. V. Chibisov reported on the untenability of Sheppard's theory of light-sensitive centers of silver sulfide. On the basis of his experimental results, obtained in conjunction with A. A. Mikhailov and A. A. Titov, he has concluded that the effect of chemical sensitization by sulfur compounds observed by Sheppard is not only inaccurately described, but is essentially incorrect, and hence the theory put forward by him in 1925 and widely accepted must be considered altogether invalid. As the lecturer showed, sulfur compounds accelerate chemical ripening only in so far as they are able to accelerate the reduction process, which has a direct effect on the changes in the photographic properties of the emulsion during the second ripening stage. As regards the mechanism of the acceleration of chemical ripening, the observed acceleration is evidently due to increase in the reactivity of silver ions in the crystal lattice near to the silver center, which results from the adsorption of "accelerator" molecules at bromide-ion sites.

I. M. Ratner, speaking for himself and on behalf of A. A. Titov, read a paper on the part played by internal centers formed when the emulsion is illuminated during ripening. The observed desensitizing action of internal silver centers agrees well with the earlier observation of K. V. Chibisov, A. A. Titov, and A. A. Mikhailov. The mechanism of this reaction is to be explained by the competition between internal and surface centers for the capture of photo-electrons. It was shown also that the formation of metallic silver by exposure of the photographic emulsion in the first ripening stage leads to diminished sensitivity only in the beginning stages, and with increased illumination the sensitivity is found to rise again. The results obtained are of fundamental importance for the understanding of the role of internal centers.

The properties of photographic layers that have been subjected to continuous illumination for varying times, or to periodic illumination, were the subject of a paper by A. L. Kartuzhansky. It was found that the laws observed for discontinuous illumination were basically similar to those observed for continuous illumination. At the same time, quantitative differences between the two effects and also a number of peculiarities observable with discontinuous illumination point to the existence of differences in the mechanisms of the two phenomena. These differences, as might be supposed, are connected with the fact that the process of latent-image formation continues also during the dark intervals.

In I. M. Roikh's paper, the question of the effect of hydrogen peroxide vapor on the latent image was considered. It was shown that, according to the exposure, the effect of hydrogen peroxide could be not only of an intensifying nature, but also of a reducing nature; this effect is evidently connected with the two ways (oxidizing and reducing) in which hydrogen peroxide can function.

The comparative effects of electrons and of light on photographic layers were treated by S. G. Grenishin. It is found that for a layer of low sensitivity to electrons the latent-image centers formed are similar to those formed by a short and intense exposure to light, whereas for a layer of high sensitivity to electrons the latent-image centers formed are similar in properties to those formed by prolonged and feeble illumination.

B. A. Barshchevsky read a paper on the quantum yield in photochemical and photo-electrical processes in silver halides, and he criticized the methods of calculating quantum yield used previously (Hilsch and Pohl, le Feld). In this paper, however, there were no convincing theoretical generalizations, and also no experimental data were cited.

Two sittings were devoted to discussion of problems of optical sensitization. A considerable proportion of the papers was concerned with the mechanism of optical sensitization. E. K. Putseiko, speaking on behalf of A. N. Terenin and of himself, read a paper on the sensitization by dyes of the internal photo-effect in semiconductors (ZnO, ZnS, TlCl, TlBr, TlI, AgCl). The condenser method, which permits the detection of the positions of local levels in the semiconductors and also the tracing of the accumulation of electrons in them, was used in this work. The semiconductors investigated have their own photoelectric sensitivity in the near ultraviolet and in the short-wave region of the visible spectrum. As a result of adsorption of dyes, photo-effect maxima appear in the visible region of the spectrum which cannot be attributed to dye microcrystals precipitated on the surface of the semiconductors and is due to adsorbed molecules. It was shown further that the photo-effect in the sensitization region shows a considerable temperature coefficient, whereas the sensitivity peculiar to the semiconductor itself changes insignificantly with temperature. It was shown also that the sensitizing effect (for TlI) depends on the concentration of F-centers in the semiconductor. Thus, the experiments show the possibility of electron exchange and accumulation of electrons in a crystal due to light absorption by molecules localized on its surface, which is a fact of great interest for the theory of optical sensitization.

Yu. N. Gorokhovsky reported on work that he had carried out in conjunction with B. V. Barbarin and E. I. Ozhereleva concerning the relation between adsorption of sensitizers, light absorption, and light-sensitivity in sensitized photographic layers. For the experiments, emulsion crystals, separated from photographic emulsions by fractional centrifugation, were used. It was found that the adsorption of the sensitizing dyes depends on the dimensions of the emulsion crystals (increases with decrease in dimensions), on the composition of the solid phase (increases on going from silver chloride, through bromide, to iodide), and on the duration of the chemical ripening of the emulsion. It was found also that the spectral sensitivity curves and the light-absorption curves for the adsorbed dyes (with the exception of erythrosine) coincided. It was concluded on the basis of the experimental results that the structure of the adsorbed layer depends not only on the initial state of the dye in solution, but also on changes in this state in the adsorbed layer, depending on the degree of adsorption. Work on the adsorption of sensitizers on pure silver bromide was reported by K. S. Lyalikov and Z. L. Petrushkina. It was shown in this work that a monomolecular layer of sensitizer is adsorbed irreversibly on silver bromide.

S. V. Natanson read a paper on the quantum yield of the sensitized photolysis of silver bromide. Quantum yields were determined for a number of dyes for wavelengths 436 and 578 mμ, which correspond to the sensitivity of silver bromide itself and to the sensitivity band of the molecular state of the dye in

solution. It was found that the quantum yield of photolysis in the band of the intrinsic sensitivity of silver bromide is somewhat changed in presence of the dye, which does not absorb in this region of the spectrum. The quantum yield is the less, the stronger the tendency of the dye to show a desensitizing effect. Quantum yields of photolysis in the sensitization band bear a definite relation to the photographic efficiency of the dye.

A. V. Borin read a paper on the effect of gelatin on the absorption spectrum of a benzthiacarbocyanine dye. The dye showed a long-wave absorption band (I-band) and a short-wave absorption maximum (β-band). For various gelatins the intensities of these bands varied appreciably, and various fractions of gelatin obtained by fraction dissolution of gelatin in water differed in their effects on the two bands referred to. The relative intensities of these bands depended also on the interaction of the gelatin gels with the silver bromide surface (both pure and containing Ag_2S). The results obtained were interpreted in terms of interaction of the dye with gelatin molecules. Questions concerning the synthesis of optical sensitizers and the relation between structure and sensitizing propensity in dyes were examined in papers by E. D. Sych and I. I. Levkoev.

E. D. Sych, speaking on behalf of A. I. Kiprianov, made a report on the work of the Institute of Organic Chemistry of the Ukrainian S.S.R. Academy of Sciences on the synthesis of photosensitizers. The Institute has carried out a great volume of work on the synthesis of dyes of various classes. The investigations on dyes have revealed the great significance of steric hindrance in dye molecules with respect to its effect on color and other properties, including the sensitizing propensity of the dyes.

I. I. Levkoev lectured on the relations between structure and photographic activity in sensitizing dyes. Taking numerous examples of dyes synthesized in the laboratory directed by the lecturer, the dependence of the sensitizing properties of dyes on their structures was examined. The effect of substituents both in the nuclei and in the polymethin chain, the effect of the length of the polymethin chain, the structures of the heterocyclic nuclei, and so on were traced. The lecturer pointed out also the great importance of the basicity of the dyes for sensitizing effect (fogging action in the case of high basicity and desensitizing action in the case of low basicity). Also at the sittings devoted to optical sensitization, I. I. Breydo reported on the question of the effect of optical sensitization on the resolving power of emulsions.

Three sittings were devoted to problems concerning photographic development. G. P. Faerman gave two papers. The first of these, which was in the nature of a review, was devoted to the present state of the electrochemical theory of development. This theory, which has been developed systematically over a long period by the lecturer and his coworkers (S. G. Bogdanov, V. A. Veydenbakh, A. I. Kan-Kogan, S. I. Cherbov, and N. N. Shishkina) has succeeded in explaining a considerable number of facts concerning the relations between the properties of developers and their compositions and also certain questions relating to the mechanism of development. In the second paper, G. P. Faerman, on the basis of experiments carried out in conjunction with E. D. Voeykova, examined the mechanism of the catalytic action of development centers. On the basis of electrochemical concepts it was suggested that catalytic action in the development process would be shown by metals or by compounds that possess electronic conductance. Experiment has confirmed this suggestion for the reduction of silver nitrate by certain developing agents.

In S. G. Bogdanov and N. V. Polyakov's paper, the significance of the buffering action of the developing solution in the development process was considered. Experiments have shown that developers of similar composition, but with differing acid-base buffer reserve, do not behave in the same way in use, the developers with low buffer reserve having "leveling-out" properties. The work has shown also that the composition of the developer in the layer may, owing to exchange difficulties, be different from that in the outside solution, and this also is related to the buffer reserve of the developer, and it is of great importance for the results of development.

N. N. Shishkina read a paper on the dependence of the developing process on temperature. She showed that the fundamental postulates of electrochemical theory were applicable also in investigations on the dependence of development on temperature, in as much as they enable various developers, which guarantee constant results independent of temperature, to be made up by calculation.

K. S. Lyalikov, on his own behalf and on behalf of V. N. Piskunova, read a paper on a microphotographic investigation of the development process. The authors attempted to solve by this method the question of the part played by the solvent in the developer and to determine absolute rates of the growth of the silver crystal during development. The results obtained throw considerable doubt on whether reaction proceeds via the solution in normal chemical development. For the solution of the second question a statistical method of investigating the developed microcrystals of silver bromide was worked out. It was found that the development of the grain has an autocatalytic character, with a dwindling in rate, however, towards the end of the development of the grain.

V. I. Sheberstov read a paper on investigations into the kinetics of the development of photographic layers. It was shown that a unimolecular reaction equation can be applied satisfactorily to the rate of image development only in special cases when working with developers of high selective action. The development of fog often follows closely to a straight line law, which is to be explained by the formation of fog centers during development. In order to explain the experimentally observed dependence of development rate on time, the lecturer brought forward theoretical considerations that took into account the distribution of latent-image specks of varying activity within the grains and the autocatalytic character of the development of an individual grain.

N. M. Zyuskin read a paper on the dissolution of silver bromide in the course of photographic development. The experiments consisted in bringing silver images and photographic layers impregnated in developer into contact; the photographic layers were afterwards developed. Dissolution of silver bromide was to be observed in places in the photographic layer that had been in contact with the silver of the image, while the image was intensified in these places. This work points to the importance of diffusion processes and of the solubility of silver bromide in the development process.

All the papers gave rise to lively discussions.

When the work of the conference had been completed, a resolution was passed. In this resolution it was pointed out that deeper investigation into the essentials of the photographic process has not only permitted Soviet chemico-photographic, cinematographic, and optical industry to be brought to the technical level of the corresponding branches of industry of the large capitalist countries, and even into a leading place in individual questions, but also created the prerequisites for the further powerful development of

these branches of industry. The progress of theoretical work in the photographic field in the U.S.S.R. is to be explained above all by the complex and planned character of the scientific investigations, which are carried out in close co-ordination with the demands of industry. The progress of theoretical investigations in photographic science results to an appreciable extent also from work done in allied branches of physics and chemistry.

The conference, in its resolution, took note of the very important problems that stand before workers in the field of theoretical photography:

1. Further study of the nature of the fine structure of the absorption spectra of photochemically colored silver halides, which was discovered by E. A. Kirillov and his coworkers. Development of work on the comparison of photochemical and photoelectric sensitivity in silver halides and the elucidation of the nature of color centers and of their relation to photographic sensitivity. Further development of investigations into the nature and origin of sensitivity centers in the crystals of photographic emulsions. Initiation of investigations into the photographic action of various radiations over a wide interval of wavelengths.

2. Carrying out investigations of the quantum yield in the regions of intrinsic and of sensitized sensitivity of photographic emulsions. Development of work both on the mechanism of optical sensitization and also on the sensitizability of photographic emulsions. Initiation of investigations directed toward the establishment of the relation between the structure of sensitizers, their physicochemical properties, and their sensitizing action.

3. Investigation of the mechanism of the catalytic action of silver in the development process. Study of the kinetics of the development both of separate emulsion crystals and of the photographic layer as a whole. Study of the effect of diffusion processes on photographic development. Investigation of the effects of various factors on the final results of photographic development.

Attention was drawn in the resolution to the delay in the publication of the transactions of conferences and discussions organized by the Committee on Photographic and Cinematographic Science. The conference found it necessary to recommend in the resolution that the Bureau of the Committee on Photographic and Cinematographic Science of the Academy of Sciences of the U.S.S.R. should again make a petition regarding the organization of a special journal on photographic and cinematographic science.